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Monica Pinheiro Feitosa

Memcapacitors

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Electrónica e Telecomunicações, realizada sob a orientação científica do Dr. Luís Filipe Mesquita Nero Moreira Alves (orientador), Professor Auxiliar do Departamento de Electrónica, Telecomunicações e Informática da Universidade de Aveiro, e do Dr. Ernesto Fernando Ventura Martins (co-orientador), Professor Auxiliar do Departamento de Electrónica, Telecomunicações e Informática da Universidade de Aveiro.

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o júri

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palavras-chave

Memcapacitores, Sistemas memcapacitivos, curvas de histerese, carga, tensão, MATLAB, simulações, funções de janela, Teorema de Green, área.

resumo

O presente trabalho propõe-se a continuar o estudo dos dispositivos de memória, iniciado com a predição dos memristors por Leon Chua em 1971, por meio do estudo e caracterização dos memcapacitores como dispositivos semicondutores de dois terminais, caracterizados pela relação não linear entre carga e tensão, que apresentam capacidade de recordar a tensão ou corrente que passa pelo dispositivo, graficamente representado em forma de um gráfico com características de histerese, aprensentando também capacitância variável em função da carga aplicada em seus terminais.
Aqui, uma caracterização das funções de resposta a uma entrada periódica sinusoidal com frequência variável, para três modelos matemáticos de sistemas memcapacitivos, é realizada: dado um memcapacitor em série com uma tensão de entrada ac, estuda-se as respectivas funções de histerese carga-tensão por meio de simulação em MATLAB.
Em seguida, é realizada uma classificação das curvas de histerese em função da sua geometria, em que a passagem do gráfico no ponto (0,0), de origem dos planos, o define como tipo I ou tipo II.
A análise prossegue com a identificação morfológica da área das curvas de histerese obtidas dos primeiro modelo teóricos em causa, variando-se, para isso, amplitude e frequência de entradas, de modo a se comparar os outros dois modelos restantes com este modelo ideal, ao mesmo tempo em que se deseja obter as frequências críticas de cada modelo, ou seja, as frequências e amplitudes a partir das quais a memcapacitância torna-se constante, e o sistema em causa, linear, fazendo então a curva de histerese degenerar para uma reta.

A área do primeiro modelo foi calculada através de um algoritmo que calcula a área da curva por meio do Teorema de Green.

keywords

Memcapacitors, memcapacitive systems, hysteresis plots, charge, voltage, MATLAB, simulations, window functions, Green Theorem, area.
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abstract

The present work aims to continue the study of memory devices, initiated with the prediction of the existence of memristors by Leon Chua in 1971, with the study and characterization of memcapacitors as a semiconductor two-terminal device, characterized by the non-linear relation between charge and voltage, which also present the ability to remember the voltage or charge that passes through the device, graphically represented by a graphic with hysteresis characteristics, also presenting a variable capacitance in function of the charge applied in its terminals.

Here, a characterizationof the response functions to a sinusoidal periodic input with variable frequency to three mathematical models of memcapacitive systems is performed: given a memcapacitor in series with an ac input voltage source, the respective hysteresis charge-voltage plots are studied by simulations in the MATLAB environment.

Next, a classification of the hysteresis plots in function of its geometry is performed, given that the crossing of such graph in the (0.0) point defines it as a type I or type II hysteresis loop.

The analysis continues with the morphological identification of the area of the hysteresis curve of the first model, by varying amplitude and frequency of the input source, in such a way to compare the other models with the ideal one, as well as to take the critical frequencis from which the memcapacitance becomes constant, and thus the system becomes linear, by making the hysteresis curve to become a straight line.
The area of the first model was taken by calculations with the Green theorem.

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1.1. Motivation

The effects of electromagnetism and the human perception of the electromagnetic forces are known since the a.C. Greek civilization, by the observations of philosophers such as Tales of Miletus, but only since the XVIII century it reached the condition of experimental science, by having its laws described by the scientific method, through experiments conducted by names such as Benjamin Franklin, Charles Coulomb, Alessandro Volta, André-Marie Ampère, Georg Simon Ohm, among many others.

However, the XIX century brought the establishment of a solid and almost complete description of the electromagnetic theory, by the four equations assembled and postulated by James Clerk Maxwell. His equations demonstrates that electric and magnetic forces are two complementary aspects of the electromagnetic theory, and the electric and magnetic fields associated to these forces travel through space in the form of waves at a constant velocity. Because of the completeness of his work, many devices were created and the theory encountered acceptance and development, in such a way that nowadays it constitutes one of the most advanced field of human knowledge.

The very basis of the electromagnetic theory can be viewed by the definition of the four fundamental variables: the current i, the voltage v, the charge q and the flux linkage φ, and their two by two combinations, from six different pairs that can be formed from these four variables, which describe the three classes of basic circuit elements - resistors, capacitors and inductors. From these fundamental quantities, the whole theory lays its foundations and can be further developed (L. Chua, 1971) (L. O. Chua, 2012):

$$\{(i,q),(v,\varphi),(v,i),(v,q),(i,\varphi),(\varphi,q)\} \tag{1.1}$$

The first two of them define the relations:

$$i(t) = \frac{dq}{dt} \tag{1.2}$$

Which defines current and relates the pair(i,q); and

$$v(t) = \frac{d\varphi}{dt} \tag{1.3}$$

Which defines voltage and relates the pair (v,φ), also known as Faraday’s Law.

Some of the devices described by the electromagnetic theory are described by the other three relationships, which define the axiomatic definitions of the common two-terminal circuit elements used in electronics, the resistor, the capacitor and the inductor, with known physical laws and vastly used in the analog and digital electronics field. Actually, the understanding and use of these three lumped circuit elements are the backbone of all electronic research and industrial applications.

The linear time-invariant resistor, defined by a relationship between v and i; in other words, by a pair (v, i), expressed by the relation $v(t) = Ri$, being R a constant quantity measuring the resistance of the resistor;

The linear-time invariant inductor, defined by the relationship between φ and i, or, in other words, a variable pair (i, φ), expressed by $\varphi = Li$; in this case, L is a constant quantity measuring the inductor's inductance;

Finally, the linear time-invariant capacitor, defined by a relationship between q and v, or, in other words, a variable pair (v, q), expressed by $q = Cv$, having C as a constant quantity measuring the capacitor's capacitance, and relates the pair (v, q) (L. Chua, 1971) (L. O. Chua, 2012).

In the XX century, however, a researcher named Leon Chua noticed a lack of symmetry in Maxwell's equations, which led to a paper in 1971 where a new approach to the field was proposed. Chua noted that, in order to obey a symmetry in the treatment of the variables, there must be a missing theoretical model for the relationship between $\varphi \; and \; q$, the same way the other variables relate to each other.

The first two pairs $(v, \varphi) \; and \; (i, q)$ from the six combinations are already related via $\varphi(t) and \; q(t)$ respectively, and are not constitutive relations because they cannot predict the corresponding current *i(t)* and voltage *v(t).* However, the last pair (φ, q) defines yet another constitutive relation since given any admissible signals $(\varphi(t), q(t))$, the corresponding $(v(t), i(t))$ can be recovered through $\varphi(t)$ and $q(t)$. From logical consistency, and symmetry considerations, it is necessary to define a fourth circuit element via the constitutive relation

$$f_M(\varphi, q) = 0 \qquad (1.4)$$

Between the variables $\varphi \; and \; q$. This element was postulated and named the memristor, acronym for memory resistor. A physical approximation if such an element has been fabricated in 2008 as a TiO_2 nano device at HP.

The common usage of the $i - t$ or $v - t$ plane (current or voltage as a function of time) by engineers and researchers also led to an overlook in these missing relations. Since it was not common to observe the behavior of Lissajous figures of magnetic flux, charge, voltage or current, links between these variables remained undiscovered.

The undiscovered relationship between charge and flux led to the prediction of a system which should display memory characteristics, remembering the charge, voltage or current that passed through it. It should describe and model several other biological and natural systems encountered in nature which show similar behavior. Such mathematical system was then called a memristor, from the junction of the words *memory* and *resistor*, once it should hold properties of a nonlinear resistor with memory. Since then such approach remained an academic curiosity, once no physical device was discovered to support the theory.

In 2008, a group at HP came up with a physical approximation of a *memristor* device and reopened interest for such element. Soon the academic world developed the idea of a memristor in several papers describing its operation, physical laws and applications, although no real device was yet launched in the market (L. O. Chua, 2012).

Among several other memristive characteristics, further described in this work, it can be highlighted the memresistance M as a nonlinear charge-dependent variable resistance which exhibit hysteretic properties, maintaining the resistance unit. The relation between charge and magnetic flux of a memristor degenerates into a resistance when the input frequency reaches very high values.

The idea of a passive device with memristive behavior should be extended for other classes of elements with memory based on the characteristics of a capacitor and an inductor, thus named, respectively, a *memcapacitor* and a *meminductor* (L. O. Chua, 2012). The description, characterization, modeling and propotyping of memcapacitors and meminductors constitute a new and cutting edge frontier of scientific knowledge yet unexploited.

Generally, the relation between current and voltage defines a memristive system, while the relation between charge and voltage specifies a memcapacitive system, and the flux-current relation gives rise to a meminductive system.

There are other ways to define the four basic elements predicted by the electromagnetic theory, namely:

Let $|\alpha|\ and\ |\beta|$ integers. They define an infinite family of circuit elements by the element code

$$(v^{(\alpha)}, i^{(\beta)}) \tag{1.5}$$

Simply referred as an (α, β) element.

A resistor is also defined as the pair $(\alpha, \beta) = (0,0) = \left(v^{(0)}, i^{(0)}\right)$ (1.6)

A capacitor is defined as the pair $(\alpha, \beta) = (0, -1) = \left(v^{(0)}, i^{(-1)}\right)$ (1.7)

An inductor is defined as the pair $(\alpha, \beta) = (-1,0) = \left(v^{(-1)}, i^{(0)}\right)$ (1.8)

And a memristor is defined as the pair $(\alpha, \beta) = (-1, -1) = \left(v^{(-1)}, i^{(-1)}\right)$ (1.9)

Two other elements are defined by such relation, namely

A memcapacitor: $(\alpha, \beta) = (-1, -2) = \left(v^{(-1)}, i^{(-2)}\right)$ (1.10)

A Meminductor: $(\alpha, \beta) = (-2, -1) = \left(v^{(-2)}, i^{(-1)}\right)$ (1.11)

For each (α, β) element, a complexity metric χ can be associated by the definition

$$\chi \triangleq |\alpha| + |\beta| \tag{1.12}$$

This way, $(\alpha, \beta) = (0{,}0) \Rightarrow \chi(0{,}0)$ =0 is a resistor; (1.13)

$(\alpha, \beta) = (0, -1) \Rightarrow \chi(0, -1)$ =1 is a capacitor; (1.14)

$(\alpha, \beta) = (-1{,}0) \Rightarrow \chi(-1{,}0)$ =1 is an inductor (1.15)

$(\alpha, \beta) = (-1, -1) \Rightarrow \chi(-1, -1) = 2$ is an memristor (1.16)

$(\alpha, \beta) = (-1, -2) \Rightarrow \chi(-1, -2) = 3$ is an memcapacitor (1.17)

$(\alpha, \beta) = (-2, -1) \Rightarrow \chi(-2, -1) = 3$ is an meminductor (1.18)

Where the following notations for voltage and current turns to be necessary:

$$v^{(\propto)}(t) \triangleq \begin{cases} \dfrac{d^{\alpha} v(t)}{dt^{\alpha}}, if\ \alpha = 1,2, \dots, \infty \\ v(t), \quad if\ \alpha = 0 \\ \int_{-\infty}^{t} v(\tau) d\tau\, , if\ \alpha = -1 \\ \int_{-\infty}^{t} \int_{-\infty}^{\tau|\alpha|} \dots \\ \int_{-\infty}^{\tau_2} v(\tau_1) d\tau_1 d\tau_2 \dots d\tau_{|\alpha|}\, , if\ \alpha = -2, -3, \dots, -\infty \end{cases} \tag{1.19}$$

And

$$i^{(\beta)}(t) \triangleq \begin{cases} \dfrac{d^{\beta} i(t)}{dt^{\beta}}, if\ \beta = 1,2, \dots, \infty \\ i(t), \quad if\ \beta = 0 \\ \int_{-\infty}^{t} i(\tau) d\tau\, , if\ \beta = -1 \\ \int_{-\infty}^{t} \int_{-\infty}^{\tau|\beta|} \dots \\ \int_{-\infty}^{\tau_2} i(\tau_1) d\tau_1 d\tau_2 \dots d\tau_{|\beta|}\, , if\ \beta = -2, -3, \dots, -\infty \end{cases} \tag{1.20}$$

Where α and β are integers.

From a mathematical perspective, the larger the complexity metric, the higher is the dimension of the state space and the larger is the number of nonlinear differential equations and exotic dynamical phenomena that can emerge.

Figure 1 shows the circuit symbols of memristor, memcapacitor and meminductor. The same symbols are used for memristive, memcapacitive and meminductive systems.The black thick line represents the asymmetry, or the polarity of the devices (Pershin & Ventra, n.d.)

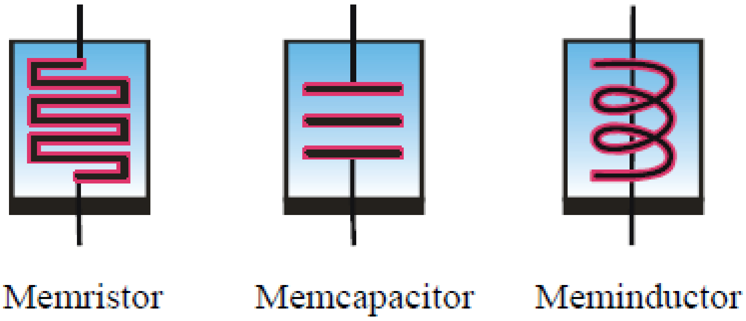


Figure 1 Memory systems devices symbols to be used in circuits (Pershin & Ventra,n.d.)

For all three devices, a convention is used to respect the device's polarization: when a positive voltage is applied to the upper terminal relatively to the terminal denoted by the black thick line, the device enters a state of high resistance, capacitance or inductance according to the one considered. Correspondingly, the device enters a state of low resistance, capacitance or inductance when a negative voltage is applied at the lower terminal (Pershin & Ventra, n.d.).

If it can be proved that a capacitor with variable capacitance exhibit characteristics of a memristive device, such capacitor may be considered a memcapacitor. This is achieved by the identification in the memcapacitive device of the three fingerprints of a memristive system.

Once in an ideal capacitor, there is a linear relationship between charge and voltage, in the form $= CV$, it is expected the characterization of a memcapacitor to be held in a q-v plane, and all the tools to identify it to be applied in such subset.

In a similar fashion, a mathematical model of a capacitor with capacitance dependent on the applied voltage may be written as $q = C(v)v$. It is expected the memcapacitance to degenerate to a linear relationship when forcing the memcapacitance to be constant, just as observed in the memresistance.

The importance of such study is not only academic, but also relies on the many applications a memristive and a memcapacitive device may assume in a near future, once physical devices are built and available. A memristor can be used in high-density memories, synapses modeling, sensors, and others. Memcapacitors can provide high and variable storage capability device with no need of an external source. Joint with memcapacitors, such devices may change the way analog electronics are handled.

1.2. General Objectives

This work has a general purpose to understand and study the memcapacitors as a new device derived from previous works on the memristors and to uncover its characteristics, contributing to the development of the field.

1.3. Specific Objectives

It will be done through the following specific objectives:

- To study the memcapacitors' dynamics of operation by documental state-of-the-art research;
- To identify the fingerprints that define a memcapacitor device by studying the behavior of the hysteretic loop when the frequency of the input signal changes;
- To define the frequency response and perform a frequency characterization of memcapacitors;
- To derive the characteristics of three types of memcapacitors through simulations;
- To derive the area of the characteristic loop of the three described models in order to give a fully quantitative characterization of the mathematical systems;
- To compare the two memcapacitive systems described.

1.4. Structure of the dissertation

This work is thus organized as follows:

- The second chapter summarizes the state-of-the art of both memristors and memristive systems, as well as it defines the fingerprints to be considered when analyzing memory systems and devices;
- The third chapter fully describes a memcapacitive system and a memcapacitor;
- The fourth chapter describes the three mathematical models used in this work;
- The fifth chapter describes the simulations performed and the results achieved;
- The sixth chapter presents the conclusions and future works to be done.

Chapter Two: Memristive Systems

2.1. Introduction

A broad definition of memory is the ability to store the state, or the information of any system at a given time, and access it at a later time. A memory state is related to some dynamical properties of the constituents of condensed matter, namely electrons and ions. This way, history-dependent features are related to how electrons and/or ions rearrange their state in a given material under the effect of external perturbations (Pershin & Ventra, n.d.).

Understanding how memory arises in physical systems demands an analysis of the properties of materials at the nanoscale. The change of state of electrons and ions is not instantaneous, and it generally depends on the past dynamics. This means that the resistive, capacitive and/or inductive properties of these systems show time-dependent features when subject to time-dependent perturbations (Pershin & Ventra, n.d.).

From both formal and practical points of view, the three traditional element relations can be generalized to time-dependent and non-linear responses. In addition, all responses may depend not only on the traditional circuit variables, such as current, charge, voltage or flux, but also on other state variables, which follow their own equations of motion and provide memory to the system. The following sections are dedicated to describe such memory elements and their relations (Pershin & Ventra, n.d.).

2.2. Systems with Memory

A memory system is any system encountered in nature that somehow remembers past stimulae, thus changing its initial conditions at each new stimulus, showing then memory capabilities. As a electromagnetic concept, it was first described by Chua and Kang as a class of device exhibiting similar behaviors, without an explicit dependence on electric and magnetic variables (Duarte, Martins, & Alves, 2013). Its physical behavior is described by the way their internal resistance, or its memristance, varies in time by its state variable.

Any condensed matter system cannot respond instantaneously to external perturbations, especially if nanoscale dimensions systems are considered, where the dynamics of a few atoms may affect the whole structure dramatically. As such, some degree of memory in the response of the system to external fields is always present (Ventra, n.d.)

This also shows that ideal resistors, capacitors and inductors are just circuit theory idealizations of actual properties of real systems, being a good representation of such properties only within a range of experimental conditions (e.g., within certain intervals of amplitudes and frequencies).

It also shows that memristive, memcapacitive and meminductive systems are simply resistors, capacitors and inductors, respectively, whose memory is made more apparent under certain experimental conditions (Ventra, n.d.).

Once resistances, capacitances and inductances are simply response functions, all other constraints introduced “artificially" in the mathematical, or axiomatic, definition of the memory elements have no reason to exist. Such unphysical constraints are the finiteness of the responses themselves at all times, with consequent crossing of the input-output curve under a periodic drive, and positiveness of the memcapacitors’ and meminductors’ response functions at all times (Ventra, n.d.)

Systems with memory can then be modeled in electric circuits as resistors, capacitors and inductors with memory, or memristors, memcapacitors and meminductors, respectively, and then used in the electronic industry the same way the other lumped circuit elements. Memristive, memcapacitive and meminductive systems are classified into current-controlled and voltage-controlled types, which, in most cases, is a matter of mathematical or experimental convenience. In particular, considering the equations describing a current-controlled memristive system, and algebraically solving it with respect to the current i, assuming a unique solution at any given time, it is possible to reach the equations of the voltage-controlled memristive system. The same happens with the other systems and classifications (Pershin & Ventra, n.d.)

Moreover, memcapacitors and meminductors can store energy in the electric and magnetic field, respectively, in addition to information, therefore opening new venues in the technologically important area of energy storage, distribution and manipulation (Ventra, n.d.)

The dynamical electrical characteristics of a memory device depend on the history the current passing through it and on the current voltage bias, requiring two equations: one that relates the voltage applied across the device and the current passing through it, and other explaining an intrinsic property called the state variable and how it changes with time (Halawani, Mohammad, Homouz, Al-qutayri, & Saleh, 2013).

It is usually typical in real systems that the response function M depends not just on the charge that flows across the system but also on one or more state variables that determine the state of the system at any given time. This could be for example the position of oxygen vacancies in TiO_2 thin films, which determines the resistance of the film on a memristor, or the temperature of a thermistor, or the degree of spin polarization in certain structures. The set of n possible state variables, related to a particular device, of which their time evolution is known is grouped in the symbol x via the differential state equation

$$\frac{dx}{dt} = f(x, i, t) \qquad (2.1)$$

Commom to all memory devices , where f is a continuous n-dimensional vector function (Pershin & Ventra, n.d.)

Based on the identification of these differential equations’ dynamics it was possible to define a complete set of formally solvable general solutions for evaluating analytically the output response for all types of ideal memory devices and systems (Georgiou, Barahona, Yaliraki, & Drakakis, 2013).

The definitions of memristive, memcapacitive and meminductive systems represent an economic way of describing a huge amount of systems, materials and devices with memory in an unified, general framework (Ventra, n.d.)

It is worth stressing that the definition embodied in the above pair of equations is not limited only to the input perturbations such as charge, current, voltage and flux. It represents any response of a given system to an arbitrary perturbation that induces memory in the output (Ventra, n.d.)

If u(t) and y(t) are any two complementary constitutive circuit variables (current, charge, voltage or flux) denoting input and output of the system, respectively, and x is an n-dimensional vector of internal state variables, we may then postulate the existence of the following nth-order u-controlled memory element as that defined by the equations

$$y(t) = g(x, u, t)u(t) \tag{2.2}$$

$$\dot{x} = f(x, u, t) \tag{2.3}$$

Where $u(t)$ and $y(t)$ are any two input and output variables, namely, current, charge, voltage or flux; g is a generalized response, x is a set of n state variables describing the internal state of the system and f is a continuous n-dimensional vector function.

2.3. Definition of the Fingerprints of a memristive device

For an element to be a memristive device, a few conditions must be fulfilled, what in the state-of-the art subset is called fingerprints. These three signature characteristics uniquely classify a device to be a memristor and distinguish them from the other non-memristive devices: a hysteresis loop, a double-valued Lissajous figure of $(v(t), i(t))$ for all times t, the decrease of the hysteresis lobe area with the increase of the frequency, and the degeneration of the loop in a linear function with high values of the input frequency (Adhikari, Sah, Kim, & Chua, 2013).

2.3.1. Hysteresis Loop

The first fingerprint to be considered as a distinctive signature of a memristive device is the hysteresis loop, a double-valued Lissajous figure of $(v(t), i(t))$ for a t axis, understood as a unique periodic steady-state solution of the state equation under any periodical bipolar input, where there exist two distinct values of v for any value of the current i.

Hysteresis loops are often associated to memory effects in elements that present such property. In a memory device, it is translated into a resistance which is able to “remember” the current or the voltage that has gone through it (Duarte, Martins, & Alves, n.d.).

Generally, such loops are very frequently reported in experimental papers when the response function $g(t)$ or the function $y(t)$, or both, are plotted versus $u(t)$. That means to say, in a memcapacitive system, a hysteretic plot can be achieved when a periodic charge $q(t)$ is plotted against a sinusoidal voltage $v(t)$ instead of generating graphs of these variables in function of time. It is then interesting to say that a hysteresis loop is an alternative way of viewing and measuring results, in opposition to the traditional way electronics engineers visualize their outcomes

The shape of the loop is determined by both the device properties and the input $u(t)$ applied. In particular, it depends on both amplitude and frequency of the input. A pinched hysteresis loop may be "not self-crossing" or "self-crossing". However, the symmetry of the state equations does not always define the type of crossing. Until now, papers dedicated to describe memristors behaviors have encountered pinched hysteresis loop passing through the origin of the axis, once, according to Ohm's law, for $i(t) = 0$ the correspondent value of voltage $v(t) = 0$ forces the loop to pass at the point $(0,0)$(Adhikari et al., 2013) (Pershin & Ventra, n.d.).

This way, two types of pinched hysteresis loops are found: type I and type II, as follows:

a) *Type I Hysteresis Loop*

Considering the case in which the hysteresis loops are well defined for generalized response functions g, meaning $g \neq 0$ and $g \neq \pm\infty$), in the sense that $y(t)$ and $g(t)$ are periodic with a period T of the applied ac voltage, the function $y(t)$ hysteresis loop passes through the origin, point where the loop is pinched, and is thus classified as type I hysteresis loop. It is the most common type of hysteresis found in memristive devices and is characterized typically by a single loop in the response g as a function of the input. Figure (2) illustrates this type of hysteresis:

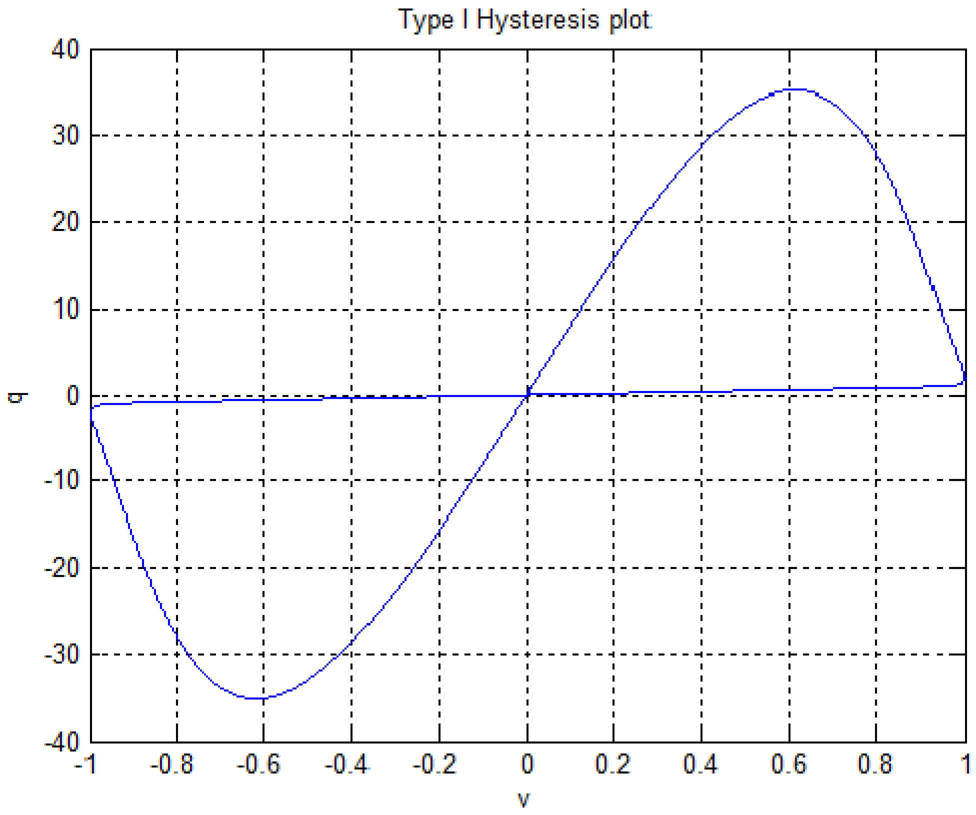


Figure 2 Type I Hysteresis Loop

b) Type II Hysteresis Loop

A type II crossing behavior results in a double loop in the response g as a function of the input. It covers several shapes of loops where they do not cross themselves in the origin of the axis, being thus presented in an elliptical form or tangentially sliding around the origin. Thus, it can be also called “non-crossing” type.

“Non-crossing” loops are very often observed when $g(x,u)$ and $f(x,u)$ are even functions of u, although this may not be a necessary condition. In the opposite case, when $f(x,u)$ is an odd function of u, “self-crossing” behavior of $y-u$ curves is more common (Pershin & Ventra, n.d.).

In situations when the response function g becomes zero or infinite when $y=0$ or $u=0$, $y-u$ curves do not pass through the origin. This is the case superlattice memcapacitive systems, and the v-i curves of the thermistor, for instance. Moreover, in some systems, additional crossing are possible at $u \neq 0$ as in the case of ionic channels. Not self-crossing loops are also observed in the case of thermistors and elastic memcapacitive systems (Pershin & Ventra, n.d.). Figure (3) illustrates this type of hysteresis plot:

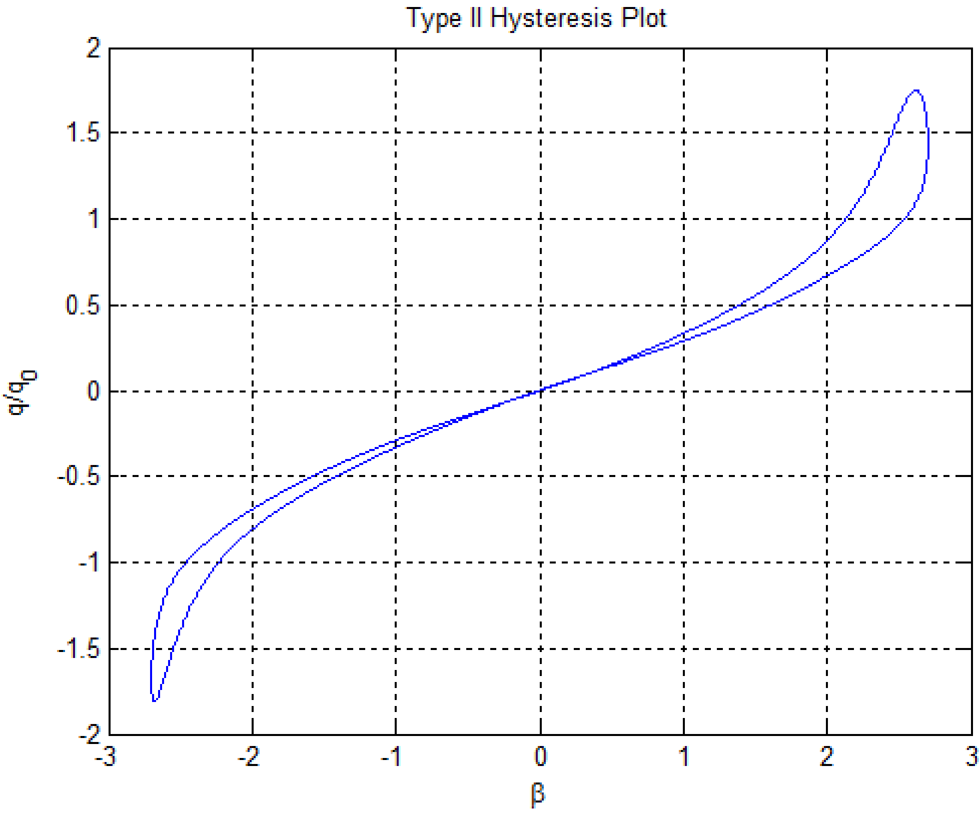


Figure 3 Type II Hysteresis Loop

For memristive devices and memristors, the hysteresis loop is pinched ate the origin$(v, i) = (0,0)$, for any possible amplitude and frequency of the input sinusoid, as well as for any initial condition of the state variables. For memcapacitors and meminductors, the (q, v) plane and the (i, φ) that respectively defines them, may present both types of hysteresis behavior.

2.3.2. Hysteresis lobe area decreases as frequency increases

The second fingerprint of a memristive device to be considered is the dependence of the hysteresis lobe area on the frequency of the periodic excitation signal. The absolute value of the lobe area of the pinched hysteresis loop should decrease monotonically above a certain critical frequency as the frequency of the periodic input voltage v(t) or input current i(t) increases (Adhikari et al., 2013).

The origin of the pinched hysteresis loop of a memory device is the approximate linearity of the state-dependent Ohm's law, where $v = 0$ if and only if $i = 0$, and vice-versa. Thus it can be seen that the hysteresis loop of a memristive device is inversely proportional to the excitation frequency. This way, the area of the hysteresis lobe, which is a direct consequence of the state variable x(t), is also inversely proportional to the excitation frequency ω (Adhikari et al., 2013).

2.3.3. Degeneration of the hysteresis curve as frequency rises

The third fingerprint to be considered is the degeneration of the hysteresis loop to a single-valued function at infinite frequency. This property asserts that even though the shape of the pinched hysteresis loop depends on the waveform of the periodic excitation voltage v(t), or excitation current i(t), they must all tend to a single-valued function through the origin, as the frequency tends to infinity (Adhikari et al., 2013)

The literature was assertive to state that, from a large range of observed memristive systems, if a device exhibits a pinched hysteresis loop, but the hysteresis lobe area does not shrink to a single-valued function with increasing frequency of the testing periodic input signal beyond its frequency, then it was not a memristive device (Adhikari et al., 2013). However, as stated before, it may not be the case for memcapacitive systems. However, the absence of a pinched hysteresis loop does not invalidate a memcapacitor to be classified as a memcapacitive device, once there are several types of identified hysteresis loops.

2.4. Are the memelements fundamental circuit elements?

For a lumped circuit element to be considered fundamental, it must be constructed without a finite combination of standard circuit elements that can reproduce the dynamical properties. In particular, it should be constructed using solid-state materials. Thus, once the behavior of an ideal memristor cannot be simulated by any combination of “standard” – namely two- terminal, time-independent, linear or non-linear – resistors, capacitors and inductors, it can be said that a memristor is a fundamental element (Pershin & Ventra, n.d.).

However, it is believed that an ideal memcapacitor also cannot be simulated by combinations of standard resistors, capacitors and inductors, because in this case as well, the lack of time dependence does not allow to retain information on the full charge dynamics. For instance, it can be thought that since standard inductors store information on the voltage history, through the integral of the voltage on the inductor, they could be used to simulate the behavior of memcapacitors. However, if this were the case, the resulting circuit would have inductive components and therefore would not be an ideal memcapacitor (Pershin & Ventra, n.d.)

Therefore, it is in this sense that ideal memristors, memcapacitors and meminductors are considered as “fundamental” circuit elements for some authors, in such a way to name them as the last two the “fifth” and “sixth” circuit elements, although some authors prefer to subscribe the notion that there are only three fundamental circuit elements, resistors, capacitors and inductors, with or without memory. Other authors resist to validate such analysis and remain with the traditional classification of considering just the resistor, capacitor and inductor as the three fundamental elements (Pershin & Ventra, n.d.).

However, the above considerations cannot be extended to memristive, memcapacitive and meminductive systems because in that case, the internal state variables could have a physical origin which could be simulated by standard (possibly non-linear) circuit elements. For instance, some memcapacitive systems may be represented by a combination of basic circuit elements (capacitors and non-linear resistors), or one could envision a combination of non-linear resistors with negative differential resistance to retain the history of the voltage or current and thus simulate memristive systems. Irrespective, these types of memory elements are still of great importance since they provide a complex functionality within a single electronic structure (Pershin & Ventra, n.d.).

In summary, such a discussion is far beyond the scope of this work and should be dealt in appropriate forums, such as conferences and by peer reviews, or let further developments in nanotechnology, solid-state physics and microelectronics define the path to be considered in such matter.

This way, it can be summarized the difference between a memory system and a memory device: the first is any system which shows characteristics of memory retention and behaves as so. It can be, for instance, a biological system, or can be noted in a chemical structure. A memory device, on the other way, is an active or passive element with memory features, that can be fabricated in a semiconductor wafer and included in an analog, digital or mixed circuit in the form of an Integrated Circuit or even a discrete device (Pershin & Ventra, n.d.)

2.5. Memristive Systems and Memristors

Systems with memory are common in nature, long before the theory of memristors were developed. However, a memristor was the first device derived from the characteristics of a memristive system by the HP laboratories in 2008, while its researchers were attempting to build a new Computer Memory's architecture. It is by definition a nanoscale solid-state two-terminal elements with nonvolatile and programmable resistance, and constituted one of the latest technology breakthroughs which may have a major impact on integrated circuit industry.

If this new technology continues to be properly developed, it will cause a revolution in the way Integrated Circuits are built and used in the consumer's industry, as well as cause decreasing changes in the way power is consumed nowadays. This fact justifies a brief explanation of how such systems are mathematically organized.

2.5.1. Memristive Systems

a) Current-Controlled Memristive Systems

From (2.2) and (2.3), an nth-order current-controlled memristive system is described by

$$v(t) = R_M(x, i, t)i(t) \qquad (2.4)$$

$$\dot{x} = f(x, i, t) \qquad (2.5)$$

Where x is a vector $x = \{x_1, x_2, \ldots, x_N\}$ representing n internal state variables, $v(t)$ and $i(t)$ denote the voltage and current across the device, and R is a scalar called the memristance, with the physical units of ohm, and needs to be solved together with equation (2.4) for the state variables dynamics.

b) Voltage-controlled Memristive Systems

From (2.2) and (2.3), an nth-order voltage-controlled memristive system is described by

$$i(t) = G_M(x, v, t)v(t) \qquad (2.6)$$

$$\dot{x} = f(x, v, t) \qquad (2.7)$$

Where $x = (x_1, x_2, \dots, x_n)$ are states variables which do not depend on any external voltages or currents, and G is called the memductance (for memory conductance), with units of Siemens.

2.5.2. Ideal Memristors

a) Charge-controlled memristor

The equation of the voltage for a charge-controlled memristor is a particular case of (2.4) and (2.5) when M depends only on charge, and, by an axiomatic approach, can be derived as follows:

$$\varphi = f(q) \tag{2.8}$$

$$\frac{d\varphi}{dt} = \frac{df(q)}{dt} \tag{2.9}$$

$$\frac{d\varphi}{dt} = \frac{df(q)}{dq}\frac{dq}{dt} \tag{2.10}$$

$$v = M(q)i(t) \tag{2.11}$$

$$v(t) = M\left[\int_{-\infty}^{t} i(\tau)d\tau\right]i(t) \tag{2.12}$$

Where

$$M(q) = \frac{d\varphi}{dq} \tag{2.13}$$

$$M(q) = \frac{\frac{d\varphi(t)}{dt}}{\frac{dq(t)}{dt}} = \frac{v_M(t)}{i(t)} \tag{2.14}$$

Is called the incremental memristance, in units of ohm. The charge is related to the current via time derivative $i = dq/dt$. It represents the ideal memristor (Massimiliano, Ventra, Pershin, & Chua, 2009)

b) Flux-controlled memristor

Let the axiomatic definition of a flux-controlled memristor be:

$$q = f(\varphi) \tag{2.15}$$

$$\frac{dq}{dt} = \frac{df(\varphi)}{dt} \tag{2.16}$$

$$\frac{dq}{dt} = \frac{df}{d\varphi}\frac{d\varphi}{dt} \tag{2.17}$$

$$i(t) = W(\varphi)v(t) \tag{2.18}$$

Where

$$W(\varphi) \equiv \frac{dq(\varphi)}{d\varphi} \tag{2.19}$$

$$W(\varphi) = \frac{\frac{dq}{dt}}{\frac{d\varphi}{dt}} = \frac{i(t)}{v(t)} \tag{2.20}$$

Is the incremental memductance in accordance to its conductance unit.

$$i(t) = W_M\left[\int_{-\infty}^{t} v(\tau)d\tau\right]v(t) \tag{2.21}$$

Equations (2.12) and (2.21) explicit the memory features of a memristor: the dependency of past values of current and voltage, respectively, in a cumulative way, taking also in consideration the initial values of these variables in the characterization of the device.

The value of the memductance, at any time t_0 depends respectively upon the time integral of the memristor current from $t = -\infty$ to $t = t_0$ Hence, while the memristor behaves like an ordinary resistor at a given instant of time t_0, its resistance depends on the complete past history of the memristor current. Such argument is also valid for the memristor memductance, once it is dependent of the time integral of its voltage from $t = -\infty$ to $t = t_0$. This means that the memristor's conductance depends on the history of the memristor voltage.

This is the argument that justifies the name *memory resistor* of this new device.

Once the memristor voltage *v(t)* or current *i(t)* is specified, the memristor behaves like a linear time-varying resistor. In the very special case where the memristor ϕ-q curve is a straight line, we obtain M(q)=R or W(ϕ)=G, and the memristor reduces to a linear time-invariant resistor, as already predicted if considering the fingerprints a memristor obeys (L. Chua, 1971)

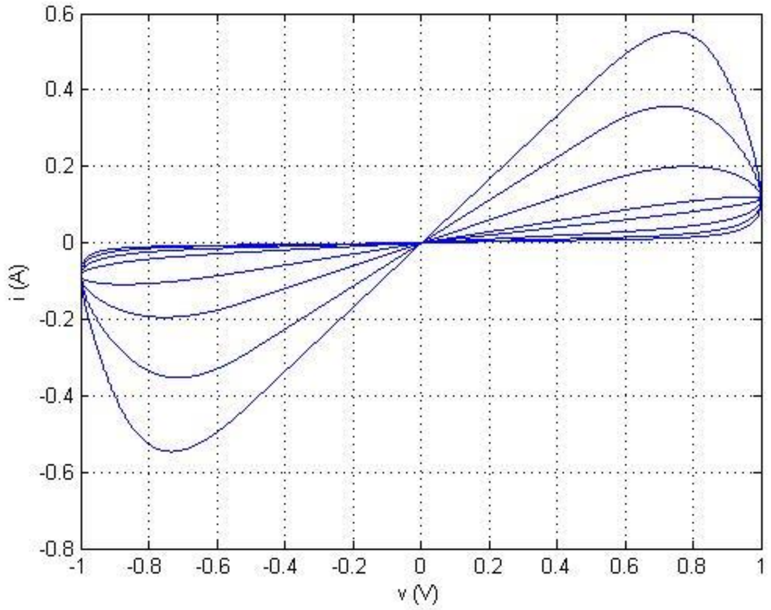


Figure 4 A typical memristor hysteresis loop, where it is explicit the dependence of loop area with increase of frequency.

2.6. Properties of memristors and memristive systems

Among the several relevant properties in the identification of memristors and memristive systems, the most important one is the appearance of a "pinched hysteretic loop" in the current-voltage characteristics of these systems when subject to a periodic input. This is a consequence from equations (2.11) and (2.18), which states $v(t) = 0$ when $i(t) = 0$, and the other way around. In addition, if the state equation has a unique solution at any given time, and if the voltage or current is periodic, then during each period the I-V curve is a simple loop passing through the origin: there may be at most two values of the current given a voltage v, for a voltage-controlled device, or two values of the voltage for a given current i, for a current-controlled system (Pershin &Diventra).

Memristive resistances have the property to degenerate into normal resistances as the amplitude of the input sinusoid decreases. Peak amplitude, which is the amplitude where the loop has maximum area of the device depends strongly on device dimensions and physical properties. This characteristic is generally dependent on the device physical parameters, but also on the amplitude and frequency stimulating signals (Duarte et al., 2013).

The memristor model presented by the HP labs in 2008 is made of a thin TiO_2 layer sandwiched between two nanowire platinum electrodes with certain length 'D' and internal state variable 'w' that represents the length of the doped region.

An external bias voltage modulates the length *w* due to charge dopant drifting, thus changing the device's total resistivity. If the dopant region w extends to full length D, the total resistivity of the device will be dominated by low resistive region and corresponding resistance is called R_{on}. Similarly, with opposite polarity undoped region extends to full length of the device, hence, the resistivity of the device is dominated by higher resistive region which leads to off state resistance R_{off} (Shrivastava & Singh, 2013).

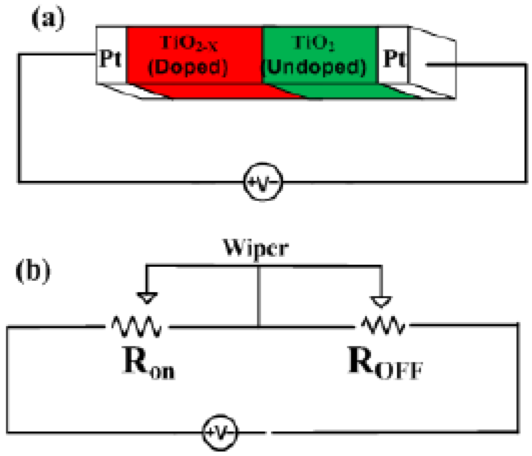


Figure 5 a) Physical structure of a memristor and b) equivalent circuit (Shrivastava, Singh)

Moreover, when subject to a periodic stimulus, a memristive system typically behaves as a linear resistor in the limit of infinite frequency, and as a non-linear resistor in the limit of zero frequency . In another words, a memristor obeys the third fingerprint of a memory device (Pershin & Diventra).

These last two properties are easily explained. Irrespective of the physical mechanisms that define the state of the system, at very low frequencies the system has enough time to adjust its value of resistance to the instantaneous value of the voltage (or current), so that the device behaves as a non-linear resistor. On the other hand, at very high frequencies, there is not enough time for any kind of resistance change during a period of oscillations of the control parameter, so that the device operates as a usual (typical linear) resistor (Pershin & Diventra).

2.7. Memristors Applications

It is expected the memristor to be applied as a logic port inside an IC. The memristor is commonly considered as an AC element, but its DC response shows spike-like dynamics that can be used to make simple logic circuits used with a novel sequential logic approach (Gale & Costello, 2013). Generally, memristors are able to perform logic operations as well as storage of information. The off-to-on resistance ratio for memristor provides adequate noise margin to separate the on versus off states (Tetzlaff, Ronald, Bruening, n.d.) (Halawani et al., 2013).

Memristors are also predicted to be used as a non-volatile memory with zero leakage current, it can be applied as a replacement for SRAM. With total compability with CMOS technology, a hybrid CMOS-memristor memory circuit would enhance the memory design, providing years of storage with zero leakage current and smaller area, thus minimizing the overall energy consumption of the system. (Halawani et al., 2013) (Elgabra et al., 2012) (Adhikari et al., 2013) (Halawani et al., 2013).

It is well known that CMOS-based memories are reaching Moore’s law upper limits, thus it is a challenger for an IC designer to meet the increasing demand for faster, smaller, and less energy consuming memory, as well as CMOS’ physical limits in achieving higher densities and lower power consumption. Memristors, however, may provide smaller size, higher utilization, and less power to operate. These are properties that can be exploited in applications with the potential of improving the performance, such as current computer memories or reconfigurable circuits and prolonging the life of CMOS technology. Actually, there is a strong possibility that the memristor may replace the CMOS technology in a near future (Elgabra, Farhat, Hosani, Homouz, & Mohammad, 2012) (Halawani et al., 2013) (Elgabra et al., 2012) (Georgiou et al., 2013)

Memristors have been compared to both neurons and synapses and have widely been anticipated as a useful route towards neuromorphic, or brain-like computing due to the its ability to hold a memory or state, by enabling the hardware implementation of large-scale neuromorphic circuits where they will be acting as the synapse in a network of neurons, emulating brain-like learning and computation (Gale & Costello, 2013) (Georgiou et al., 2013).

They can be used in future analog, digital, and mixed signal circuits as a new family of nano- scale nonvolatile memory devices, once they may replace Flash, DRAM, and SRAM in the near term. Significant industrial applications as nano-scale neuromorphic chips that would significantly outperform current neural networks. (Tetzlaff, Ronald, Bruening, n.d.) (Rose, 2010).

Memristors can be used to model the adaptative behaviour of unicellular organisms, such as amoebas, by introducing the concept of learning circuits, namely LC circuits with memristive elements, which can recognize input waveforms patterns and thus adapt to the incoming signal (Di Ventra, Pershin, & Chua, 2009)

In conclusion, driven by the potential impact of memristors, the research activity in the field has mainly focused on fabrication processes and applications of memristive devices. Unlike other conventional circuit elements, there is no established circuit theory for studying memristors as individual elements or as part of larger networks in which memristors may be combined with other circuit components (Georgiou et al., 2013)

Chapter Three: Memcapacitors

3.1. Introduction

Memcapacitive and meminductive systems are two recently postulated classes of circuit elements with memory derived and extendend from the class of memristive systems. They are special cases of (2.2) and (2.3), where their two defining constitutive variables are charge and voltage for the memcapacitance, and current and flux for the meminductance Their main characteristic is a hysteresis loop – which may or may not pass through the origin – in their constitutive variables when driven by a periodic input, and show decrease in hysteresis area with increasing frequency of the input sinusoid (DiVentra et al., 2009)

One of the main advantages from the arise of memcapacitors and meminductors in contrast to traditional capacitors and inductors is the fact that these new devices are passive ones that can store energy at the same time they hold the property to “remember” input signals.

A memcapacitor obeys the relation $q = Cv$, bein C a non-constant capacitance, and the hysteresis loop appears when plotting the C-v relation, being v the input parameter of the system. The memcapacitor may hold the capacitance due to a first voltage input until a different voltage value is applied or until the decay time of the memcapacitor is reached. If this dependence is nonlinear then there exists a switching threshold for the capacitance state and the device can be considered as a non-volatile programmable capacitor which retain a memory of past conditions may be a solid state memory device with high storage density, no power requirements for long term data retention, and fast access times (Martinez & Ventra, n.d.) (“Patent - Two Terminal Memcapacitor Device.pdf,” n.d.)(Lehtonen et al., 2013) (“Patent - Two Terminal Memcapacitor Device.pdf,” n.d.) .

As a memristive system device, a memcapacitor is completely described by a system of two equations, one of them relating the state of the system, by a differential equation, while the other describes the memcapacitance of the device.

3.2. Constitutive relations of memcapacitive systems and memcapacitors

Memcapacitive systems and memcapacitors can be defined in two ways: voltage-controlled, when values of the voltage across the memcapacitor controls the device, and charge-controlled, when values of charge controls it. This definitions, however, are merely didactic.

3.2.1. Memcapacitive Systems’ constitutive relations

In this section, a mathematical description of the memcapacitive systems is presented.

a) Voltage-Controlled Memcapacitive System

A voltage-controlled memcapacitive system is defined axiomatically by the nonlinear constitutive relation

$$\sigma = \sigma(\varphi) \tag{3.1}$$

Where

$$\sigma = \int_{-\infty}^{t} q(\tau)d\tau \tag{3.2}$$

Which, combined with equations (2.2) and (2.3), form:

$$q(t) = C_M(x, V_C, t)V_C(t) \tag{3.3}$$

$$\dot{x} = f(x, V_C, t) \tag{3.4}$$

Where $q(t)$ is the charge on the capacitor at time t, $V_C(t)$ is the voltage across the memcapacitor, and $C_M(x, V_C, t)$ is the memcapacitance which depends on the state of the system and can vary in time, defined as

$$C_M(\varphi(t)) = \frac{q(t)}{\frac{d\varphi}{dt}} = \frac{q(t)}{V_C(t)} \tag{3.5}$$

From equation (3.3) it follows that $V_c = 0 \Rightarrow q(t) = 0$, but $I = 0 \nRightarrow q = 0$, and thus it can be mathematically justified that this device stores energy.

b) Charge-controlled memcapacitive system

A charge-controlled memcapacitive system is defined axiomatically by the nonlinear constitutive relation

$$\varphi = \hat{\varphi}(\sigma) \tag{3.6}$$

Where

$$\varphi = \int_{-\infty}^{t} v(\tau)d\tau \tag{3.7}$$

Which, combined with equations (2.2) and (2.3) yields:

$$V_c(t) = D_M(x, q, t)q(t) \tag{3.8}$$

$$\dot{x} = f(x, q, t) \tag{3.9}$$

Where $q(t)$ is the charge on the capacitor at time t is, $V_c(t)$ is the applied voltage.

D_M is an inverse memcapacitance, which depends on the state of the system and can vary in time, according to the equation

$$D_M(\sigma) = \frac{d\varphi}{d\sigma} = \frac{\frac{v(t)}{dt}}{\frac{q(t)}{dt}} = \frac{v(t)}{q(t)} \tag{3.10}$$

In the above two equations, the lower integration limit (initial moment of time) may be selected as $-\infty$ or 0 if $\int_{-\infty}^{0} V_C(\tau)d\tau = 0$ and $\int_{-\infty}^{0} q(\tau)d\tau = 0$ (Pershin & Ventra, n.d.)

3.2.2. Memcapacitors' constitutive relations

Memcapacitors are a special case of memcapacitive systems when the capacitance depends only on the full history of the voltage or charge across the system. In the future, they can be brought to market as a physical device to be used in electronic systems. In this section their constitutive relations are mathematically modeled.

a) Voltage-controlled memcapacitors

A voltage-controlled memcapacitor is defined by the following equation, derived from (3.3) and (3.4):

$$q(t) = C_M\left[\int_{t_0}^{t} V_C(\tau)d\tau\right]V_C(t) \tag{3.11}$$

$$q(t) = C_M(\varphi)V_C(t) \tag{3.12}$$

The voltage-controlled memcapacitor charge and current are derived from a memcapacitive device, mathematically from equations (3.11) and (3.12) as follows:

$$\mathrm{q(t)} = \frac{\mathrm{d\sigma(\varphi)}}{\mathrm{dt}} = \frac{\mathrm{d\sigma(\varphi)}}{\mathrm{d\varphi}}\frac{\mathrm{d\varphi}}{\mathrm{dt}} = \mathrm{C_M(\varphi)v(t)} \tag{3.13}$$

$$\mathrm{i(t)} = \frac{\mathrm{d}}{\mathrm{dt}}\left(\mathrm{C_M(\varphi)V_C(t)}\right) \tag{3.14}$$

where

$$\mathrm{C_M(\varphi)} = \frac{\mathrm{d\sigma(\varphi)}}{\mathrm{d\varphi}} \tag{3.15}$$

b) Charge-controlled memcapacitors

Also called TIQ-controlled memcapacitor, a memcapacitor controlled by charge is defined axiomatically by the nonlinear constitutive relations

$$V_C(t) = D_M\left[\int_{t_0}^{t} q(\tau)d\tau\right]q(t) \tag{3.16}$$

$$V_C(t) = D_M(\sigma)q(t) \tag{3.17}$$

Where $q(t)$ is the charge on the capacitor at time t, $V_c(t)$ is the applied voltage and D_M is an inverse memcapacitance which depends on the state of the system and can vary in time. The relationships between these two constitutive variables are displayed as hysteretic loops (Martinez & Ventra, n.d.) (Lehtonen et al., 2013) (Wang, Fitch, Iu, & Qi, 2012).

The inverse memcapacitance D_M at the operating point Q can be derived from the constitutive relations as follows:

$$D_M(\sigma) = \left.\frac{d\varphi}{d\sigma}\right|_Q \tag{3.18}$$

Differentiating both sides of (3.18) yields the voltage-charge relations

$$\frac{d\varphi}{dt} = v(t) = \frac{d\hat{\varphi}(\sigma)}{d\sigma}\frac{d\sigma}{dt} = D_M(\sigma)q(t) \tag{3.19}$$

The same way, the current relation of a memcapacitor is defined as

$$q(t) = \frac{v(t)}{D_M(\varphi)}$$

$$i(t) = \frac{d}{dt}\left(\frac{v(t)}{D_M(\varphi)}\right) \tag{3.20}$$

The energy added and removed from a capacitor is defined as

$$U_c = \int_0^t V_c(\tau)i(\tau)\,d\tau \geq 0 \tag{3.21}$$

Plotting Uc versus time becomes clear that the solid-state memcapacitor operates as a dissipative device since the amount of added energy is on average larger than the amount of removed energy, resulting in positive values of Uc at all times (Martinez & Ventra, n.d.).

3.3. Properties of Memcapacitors and Memcapacitive Systems

The first property to be considered is that memcapacitors and memcapacitive systems form both types of hysteresis loops when the charge that passes through its terminals are plotted against the input voltage. A pinched hysteresis loop may occur because the definition $q = C(x)v$ imposes the graph to pass though the origin when both values of *q* and *v* are null. However, type II hysteresis plots may describe memcapacitive systems for specific mathematical models to be considered, as this present work will further demonstrate.

The hysteresis shrinks at higher frequencies, and this is the second fingerprint of a memory device, related to the fact that at high frequencies the internal degrees of freedom of a system with memory do not have enough time to respond to the external perturbation. Similarly, with increasing frequency, a decrease in capacitance hysteresis as well as in the rate of energy dissipation has been observed in theoretical works. (Martinez-Rincon, Di Ventra, & Pershin, 2010)

It follows from equation (3.3) or (3.8) that, in general, the charge is zero whenever the voltage is zero. In this case $q = 0$ does not imply $i = 0$, and vice-versa, and thus a memcapacitive system can store energy, which can be both added to and removed from the system. However, unlike memristive systems, in the present case relation 3.21 does not always hold. This implies that equations (3.3) and (3.4) or equations (3.8) and (3.9) for the memcapacitive systems may, in principle, describe both active and passive devices. In a pinched hysteresis loop, the areas of each lobe give the energies

$$U_1 = \int_0^{T/2} V_C(q)dq \tag{3.22}$$

And

$$U_2 = \int_{T/2}^{T} V_C(q)dq \tag{3.23}$$

Added to or removed from the system, respectively, when the integral runs over half of the period. The memcapacitive system can then be (Pershin & Ventra, n.d.)

Nondissipative, when $U_1 + U_2 = 0$ (3.24)

Dissipative, when $U_1 + U_2 > 0$ (3.25)

And

Active, when $U_1 + U_2 < 0$ (3.26)

A memcapacitive system can be dissipative in two different ways where a practical realization of memory capacitance is taken into account. The simplest one is via a geometrical change of the system, where a variation in its structural shape like in nanoelectromechanical systems can be used as an example. Alternatively, quantum-mechanical properties of the free carriers and bound charges of the materials composing the capacitor can be analised, giving rise, for instance, to a history-dependent permittivity ε(t). In either case, inelastic (dissipative) effects may be involved in changing the capacitance of the system upon application of the external charge or voltage control parameter. These dissipative processes release energy in the form of heating of the materials composing the capacitor (Pershin & Ventra, n.d.)

On the other hand, an active device may be realized when energy is needed from sources that control the state variable dynamics, in order to vary the capacitance. This energy is different from the control parameter, such as, for example, in the form of elastic energy or provided by a power source that controls the permittivity of the system via a polarization field. This energy can then be released in the circuit thus amplifying the current (Pershin & Ventra, n.d.).

Memcapacitive systems share with memristive systems the property that they typically behave as linear elements in the limit of infinite frequency, and as non-linear elements in the limit of zero frequency, assuming that equations (3.3) and (3.8) admit a steady-state solution. This characterizes the third fingerprint of a memory device, as already predicted once the system shows memory features. The origin of this behavior rests again on the system's ability to adjust to a slow change in bias for low frequencies, and its inability to respond to extremely high frequency oscillations (Pershin & Ventra, n.d.)

In addition, considering that the state equation (3.3) has only a unique solution at any given time $t \geq t_0$, and if $V_C(t)$ is periodic, the $q - V_C$ curve is a simple loop during a period. That means, there may be at most two values of the charge q for a given voltage V_C, for a voltage-controlled device, or two values of the voltage V_C for a given charge q, for a charge-controlled system. This loop is also anti-symmetric with respect to the origin, if, for the case of equations (3.3) and (3.8), $C(x, V_C, t) = C(x, -V_C, t)$ and $f(x, V_C, t) = f(x, -V_C, t)$ (Pershin & Ventra, n.d.).

In summary, the existence of a pinched hysteresis curve has always been declared as a signature of memristive systems, but as more development is achieved in memristive devices as well as more research about other classes of memory systems and devices appears, such as the present one about memcapacitors, it becomes very clear that a pinched hysteresis loop is neither necessary nor physically important to characterize a system with memory. The pinched hysteresis curve is simply a typical feature that may or may not be present in all devices' curves. Several research nowadays report O-shaped hysteresis curves in solid-state memcapacitive systems (Ventra, n.d.)

Therefore, from a physical point of view, the input and output signals have to be bound functions of time, but as far as the response functions are concerned, at any given time the input u(t) may be zero, while the output y(t) remains finite. From Eq. (1.2) it is obvious that the response function is infinite at that particular instant. Therefore, unlike what has been always assumed for memristive systems, there is no need to artificially enforce the response function to be finite in a memcapacitor system (Ventra, n.d.)

In addition, if the response function can acquire an infinite value at certain times, then it is not necessary that memristive, memcapacitive and meminductive systems to show “pinched" hysteresis loops: at the time when u is zero, the response g may be infinite, and therefore y is finite. Conversely, we may have situations in which at some time the response function is zero, the output y is zero, but the input is finite (Ventra, n.d.)

As an example of such, a metallic system driven into a superconducting state has its dynamics reverted to the metallic state, but following a different path. This system has memory but its characteristics curve will not pass through the origin.

Another important property refers to the sign of the response function g at any given time. For memristive systems, the condition of passivity implies that the resistance is always non-negative at all times, once a negative resistance can only be considered from an active element. However, such a condition does not preclude a change of sign of the capacitance at certain times. This can be physically understood in the way permittivity in a memcapacitive system lags behind the voltage applied to the system. In that case, at the instants of time when the voltage changes sign, the dielectric cannot fully screen this field. This under-screening effect results in the “wrong" sign of charges on the capacitor plates compared to the direction of the field, and therefore in a negative capacitance. Similar considerations can be made when the material between the plates over-screens" the field at certain instants of time (Ventra, n.d.)

3.4. Physical limitations of memelements

This section focuses on the physical limitations of memcapacitors. Although not yet implemented, research done so far can predict the drawbacks a future device may face. In order to take such limitations into consideration, it is important to note that non-volatile information storage without energy barriers that separate distinct memory states is impossible. Usually, for stability of the stored information over times much longer than any practical reading time, an energy barrier much larger than kT is required, where k is the Boltzmann constant, and T is the temperature of the environment. The models of ideal memelements do miss such barriers. Therefore, in all these cases, even very small input signals – applied for a sufficient time - can change the system state. This implies a high sensitivity of ideal memelements to fluctuations in the input variable. Being unprotected against fluctuations, internal states exhibit diffusive dynamics (similar to Brownian motion) causing the state degradation, a phenomenon that can be named as stochastic catastrophe (Ventra, n.d.)

In particular, the intrinsic thermal agitation of electrons inside any voltage-controlled memelement is responsible for the Johnson-Nyquist noise, or voltage fluctuations, which are present regardless of any applied voltage, and even in systems that are not connected to any circuit at all. The thermal voltage fluctuations thus act as an internal degradation mechanism in such devices, which in the absence of any energy barrier to protect the state of the system, leads to a diffusive loss of information (Ventra, n.d.)

Moreover, the logical (and hence physical) irreversibility of any computing machine imposes a minimal heat generation condition on any memory device. This minimal heat generation is of order kT per machine cycle, and is known as Landauer principle. Considering the switching of a memelement at constant temperature and pressure, the relevant thermodynamic potential is the Gibbs free energy, which should involve energy barriers between different information states and corresponding heat dissipation. However, the memelements' equations do not involve any restrictions on minimal switching energy, and thus violates Landauer's principle. In fact, this is simply another consequence of not having energy barriers between different memory states in any ideal memelement model. Although Landauer's principle was formulated for digital computing, the same physical constraints apply also to analog computing as well, such as the one that can be performed with memory elements.

3.5. Examples of memcapacitive systems

Although a memcapacitor has not yet been implemented, various systems exist in nature that exhibit a memcapacitive behavior, including vanadium dioxide metamaterials, nanoscale capacitors with interface traps or embedded nanocrystals, and elastic capacitors. Memcapacitive effects may also accompany memristive effects in nanostructures, since in many of them the morphology of conducting regions changes in time (Martinez-Rincon et al., 2010) (D. B. Strukov, et al, Nature, 453, 80 (2008).)

Under the term capacitor, a general electronic device capable of storing charge and energy is understood. Such a device normally includes a couple of external metal plates having negligible resistance and a dielectric medium between the plates. In capacitors, memory effects can originate from changes in the geometry and/or permittivity.

Under geometrical mechanisms of memcapacitance, situations when geometrical morphology of the plates changes in time (e.g., their relative distance and/or shape) can occur. In permittivity-related mechanisms, dielectric properties of the material between the plates provide the memory. Three most probable permittivity-related mechanisms can be then identifyed: *delayed-response mechanism*, when dielectric permittivity dynamics involves a time delay, *permittivity-switching mechanism*, when the dielectric constant changes its value under the external input (but the response is fast), and *spontaneously-polarized medium mechanism*, in which a spontaneously-polarized material (ferroelectric) is used in the capacitor structure.

It is further illustrated physical systems demonstrating these different mechanisms of memcapacitance. Known mathematical models of some of these systems are also presented.

3.5.1. An elastic memcapacitive system

A simple electro-mechanical device with memory, an elastic capacitor, can be viewed and modeled as an *elastic memcapacitive system,* once *i*t can be viewed as a parallel-plate capacitor with an elastically suspended upper plate and a fixed lower plate as shown in figure (5). When a charge is added to the plates, the separation between them changes as oppositely-charged plates attract each other. The dynamics of the system depends on initial conditions and time-dependent fields thus providing a memory mechanism.

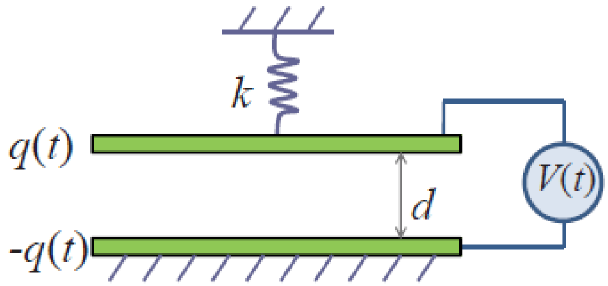


Figure 6 elastic memcapacitive system connected to a voltage source V(t)

The internal state variable y of the elastic memcapacitive system is the displacement of the upper plate from its equilibrium uncharged position d_0, under the action of a Couloumb interaction of oppositely charged plates. Mathematically, the charge dynamics on the elastic memcapacitive system is described by a parallel-plate capacitor model with variable separation between the plates

$$q = \frac{C_0}{1 + \frac{y}{d_0}} V_C \quad (3.27)$$

Where C_0 is the equilibrium capacitance at q=0, and the dynamics of y is given by the classical harmonic oscillator equation includind damping and driving terms:

$$\frac{d^2y}{dt^2} + \gamma \frac{dy}{dt} + \omega_0^2 y + \frac{q^2}{2\varepsilon_0 m S} = 0 \quad (3.28)$$

Here, γ is a damping coefficient representing dissipation of the elastic excitations,$\omega_0 = \sqrt{k/m}$, k is the spring constant, m is the upper plate's mass, S is the plate´s area. It follows from equations above that the elastic memcapacitive system is a second-order charge-controlled memcapacitive system. It is dissipative when $\gamma > 0$ and non-dissipative when $\gamma = 0$.

Previously, the model of elastic memcapacitive system was used in studies of lipid bilayers and to explain electrical breakdown of biological membranes. From the memory elements standpoint, the elastic memcapacitive system is an important example of passive memcapacitive device.

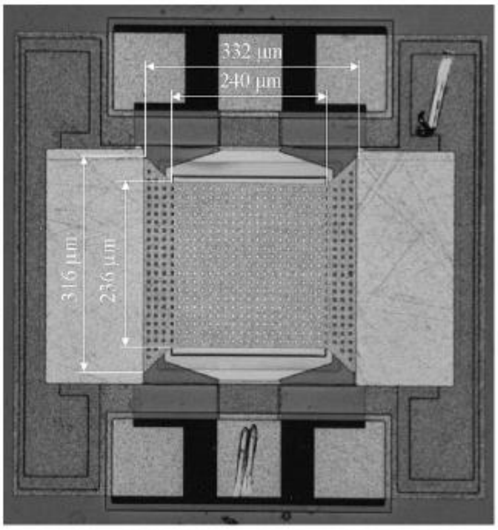
Simulations of the elastic memcapacitive system presented in scientific literature show that the upper plate oscillates when a single voltage pulse is applied to the elastic memcapacitive system, and such oscillations last for an extended period of time keeping the memory about the pulse. In the equation of motion for the state variable (3.28), the driving force is proportional to q^2, so the hysteresis q-V curves of the elastic memcapacitive system do not self-intersect at (0,0). They are then of type II, similar to the I-V curves of thermistor for a memristive system.

Once Memcapacitive systems have a hysteretic loop that may or may not be pinched, in the case of elastic memcapacitive system, the interaction force is attractive and does not depend on the separation between the plates.

3.5.2. Micro- and nano-electro-mechanical systems

Micro-electro-mechanical system (MEMS) and nano-electro-mechanical system (NEMS) capacitors are variable capacitors whose operation is based on an interplay of mechanical and electrical properties of micro- and nano-size systems. Such elements are key components in many radio-frequency applications such as tunable filters, impedance matching circuits and voltage-controlled oscillators. In addition, these structures, on the nanoscale, are considered for memory applications and sensitive measurements. Normally, capacitors built from these systems utilize a diaphragm-based, a microbridge-based or a cantilever-based structure fabricated via micromachining.

Figure 40 shows an experimental image of a memcapacitive system constructed from MEMS and measured capacitance as a function of voltage. The capacitance curve shows a well defined hysteresis which is a manifestation of memory effects in the structure. Memory effects are related to displacement of a top capacitor plate that can be considered to be suspended by a spring. Next, a model of elastic memcapacitive system that can be used to describe the capacitor features of the MEM system shown in figure (7) is considered.



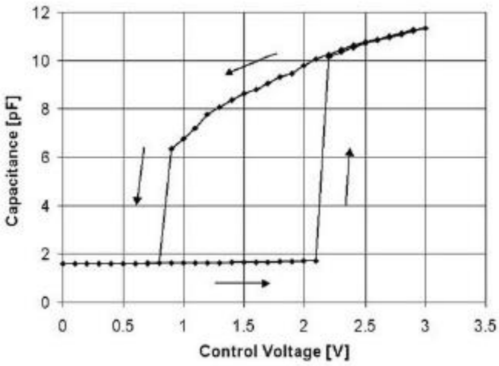


Figure 7 image of a two-state memcapacitive system constructed from MEMSm and its capacitance as a function of applied voltage.

3.5.3.Ionic memcapacitive systems

Memcapacitive behavior can be observed also in certain ionic systems because of their relatively slow dielectric response. A typical nanopore sequencing setup is an example of such a system. Two chambers with ionic solution separated by a membrane with a nanopore are considered in this model. When a varying voltage is applied to electrodes located in different chambers, ions redistribute with a time lag affecting the total system capacitance. In particular, it has been shown that the ac response of such a system demonstrates non-pinched q-V_C hysteresis loops, and both negative and divergent capacitance. Moreover, the equivalent scheme of this setup can also be modeled using a set of classical circuit elements. Since nanopores are ubiquitous on membranes of biological cells (e.g., the nerve cells) we expect these phenomena to be observable (at appropriate frequencies) even in those cases.

3.5.4. Permittivity-switching memcapacitive systems

An analog memory capacitor has been reported in Polymer-based memcapacitive systems.Its programmable capacitance was achieved in a field-configurable doped polymer, in which the modification of ionic concentration induces a nonvolatile change in the polymer dielectric properties. In this system, the $RbAg_4I_5$ ionic conductor functions as an ionic source, which contains Ag cations with higher mobility and iodine anions, whose mobility is lower. Negative voltage pulses above a threshold were used to inject iodine anions into the polymer, while positive voltage pulses above the threshold were used to extract iodine anions from the polymer. Some of Ag cations follow the iodine anions because of electrostatic interactions. When in the polymer, the anions and cations form ionic dipoles increasing the polymer permittivity and device capacitance. Since a voltage above a threshold is needed to overcome the ionic bonding with the polymer, the devices provide reasonable nonvolatile memory characteristics. In particular, it has been reported that after the analog capacitance was configured to a certain value, it changed by less than 10% under continuous reading for 5 days.

3.5.5. Phase-transition memcapacitive systems

During the process of a metal-to-insulator transition (MIT) both resistance and dielectric properties are affected. This latter property was used to fabricate a memory metamaterial in which a persistent electrical tuning of a resonant frequency was demonstrated. In this particular case, vanadium dioxide has been used as the memory material undergoing the MIT. In the experimental setup, a split-ring resonator array was patterned on a 9-nm thin film of vanadium dioxide connected by two electrodes to a voltage source. The device was mounted on a temperature-controlled stage and a temperature of 338.6 K was selected. At this temperature, the slope of the resistance as the function of temperature is the steepest because of the proximity to the MIT. Therefore, even small amplitude voltage pulses have a notable effect on material characteristics. Such electrical pulses directly applied to vanadium dioxide were used to modify its dielectric properties. The latter ones were registered by measuring the modification of the resonant frequency of the split-ring resonator array.

3.5.6. Spontaneously-polarized medium memcapacitive systems

a) Ferroelectric memcapacitive systems

Another interesting concept is the use of ferroelectric materials as the dielectric medium of a memory capacitor. Ferroelectric materials are composed of domains with a non-zero average electrical polarization. The polarization of ferroelectric materials shows hysteresis as a function of electric field, revealing two well-defined polarization states. These states are used in the ferroelectric ramdom-access memory (RAM) technology having functionality similar to Flash memory.

b) MOS capacitors with nanocrystals

Metal-Oxide-Semiconductor (MOS) structures with embedded nanocrystals have been much investigated recently. These devices are promising candidates to replace floating-gate Flash memory. The latter, in fact, has long programming times and poor endurance. Many different materials such as Si, Au and Ag have been considered as candidates for the nanocrystals that store charge. Currently, Ge nanocrystals seem to be the most promising ones because of a better data retention due to the smaller band-gap compared to Si.

It is known that C-V curves of usual MOS capacitors demonstrate a non-linear behavior. Nanocrystals added to a MOS structure provide a mechanism to control the displacement of the C-v curve. When charge is transferred to nanocrystals, this curve shifts by the amount ΔV_{FB} determined according to the equation

$$\Delta V_{FB} = \frac{-qnD}{\varepsilon_{ox}}\left(t_{CO} + \frac{1}{2}\frac{\varepsilon_{ox}}{\varepsilon_{Ge} t_{dot}}\right) \tag{3.29}$$

Where q is the elementary charge, n is the number of charges per nanocrystal, D is the density of Ge nanocrystals, t_{CO} is the control oxide thickness, t_{dot} is the mean diameter of Ge nanocrystals, ε_{Ge} and ε_{ox} are dielectric permittivities of Ge nanocrystals and oxide, respectively.

From the point of view of memory elements, the amount of transferred charge n plays the role of the state variable defining the capacitance C(V,n). Its dynamics can be described by a rate equation. However, the total equivalent scheme of such device should include a resistor in series with a capacitor as charge transfer to nanocrystals involves also dissipation processes. Indeed, such an equivalent resistor-capacitor circuit of MOS capacitors with nanocrystals do not manifest a purely memcapacitive behavior, although the memcapacitive component in these devices seems to be the dominant one.

3.6. Memcapacitors Applications

Although memcapacitive systems are well known in nature, and no electronic memory capacitor has been built yet, that can be used in electronic circuits, devices already exist that operate like memcapacitors, even if not categorized as such. Examples are a finite charging/discharging time of nanocrystals embedded in a capacitor (Pershin & Ventra, n.d.).

This happens because at nanoscale dimensions, the dynamical properties of electrons and ions strongly depend on the history of the system, at least within certain time scales. Therefore, many devices at these length scales retain partial memory of the electron and ion dynamic (Pershin & Ventra, n.d.).

In addition to the nonvolatile memory application, once they store information continuously, according to the values of the control parameter, these elements acquire a bounded continuous set of capacitances. This implies that they store analog information and, therefore, can be useful not only for conventional digital low-power computation and storage but can be used for potential applications of memory circuit elements envisioned in both analog and digital domains. This way, memcapacitors can be used for high density data storage, circuit calibration or to provide self programming, fuzzy logic, or neural learning capabilities. Aligned with these new functionalities, memory arrays can be built without the need of a power source, and it would represent a paradigm change in electronics (Di Ventra et al., 2009) (Pershin & Ventra, n.d.).

Switching devices, self-programming circuit elements, memory devices capable of multi-state storage, solid-state elements which can be used to tune circuits, analog neuronal computing devices which share fundamental functionalities with the human brain, and electronic devices for applying fuzzy logic processes are systems which could benefit from retained memory of past conditions a memcapacitor is able to provide (“Patent - Two Terminal Memcapacitor Device.pdf,” n.d.).

Another application of these memory devices can be understood in the realm of simulating and understanding biological processes and neuromorphic circuits, namely, circuits, that mimic the function and operation of biological systems. For instance, the potassium and sodium channel conductances in the classic nerve membrane model can both be identified as memristive. Memristors have been used to understand the adaptive behavior of unicellular organisms, such as amoebas, by introducing the concept of learning circuits, namely LC circuits, with memristive elements, which can recognize input waveforms patterns and thus adapt to the incoming signal.

In real systems, the three memory features – memristors, memcapacitors and meminductors - may appear simultaneously, specially at the nanoscale, the same way the three traditional lumped circuits elements are mixed in an electronic circuit (Pershin & Ventra, n.d.).

It is also known that memristive and memcapacitive effects can be simultaneously observed in the resistance switching memory cells. Experimental data show that the changes in memristance and memcapacitance are correlated and, therefore, they are most probably related to the same state variables. We thus expect that in nanoscale systems memristive behavior is always accompanied to some extent by a possibly very small capacitative behavior (Pershin & Ventra, n.d.).

Chapter Four: Case Study

4.1. Introduction

This section describes the methodology used in the present work to present a full description of a memcapacitor and its characteristics. Three mathematical models of memcapacitor were used, two of them taken from scientific papers and the last proposed by the author's adviser.

All of them were modeled using window functions. A proper justification of the use of window functions is that it causes deviations from the theoretical behavior of the simulated mem-elements, and, as a consequence, the memcapacitor passes to the more general memcapacitive system, which do not need to show the memcapacitor's fingerprints.

After properly described, the three models were compared with each other, in order to derive a complete model of a memcapacitor with its q-v characteristics.

4.2. Window functions

Window functions are functions of the state variable that forces the bounds of the device in order to model nonlinear behaviors close to these bounds. There are several window functions proposed, such as Strukov, Joglekar and Wolf, Biolek and Prodromakis.

A window function is included in the state equation in order to handle nonlinearities of the device:

$$\frac{dx}{dt} = k * q(t) * F(t) \tag{4.1}$$

Where the time derivative of the state depends on the charge in a charge-controlled memcapacitor, $F(t)$ is a window function chosen from the ones commonly used when modeling a memory device, and k is a constant derived from the device parameters.

The window function used in this work is the Prodromakis Window Function, described as:

$$f(x) = 1 - [(x - 0.5)^2 + 0.75]^p \tag{4.2}$$

This window function scales upwards, which implies that $0 < f_{max}(x) < 1$. The variable p can take any positive real number, allowing a greater extent of flexibility. P is a control parameter that co-determine both the rate of decrease of the window function as the state variable approaches its bounds and the maximum value of the function itself. It can assume any real positive number and has the function to control the non-linearity of the model where it is applied, as well as the values range of the window function. In the present work p was assumed to have the constant value of 10. The boundary issues are also resolved with the window function returning a zero-value at the active bi-layer edges (Adzmi & Herman, 2012)

4.3. Green’s theorem and area of the hysteresis loops

Baptized under the name of the British mathematician George Green, who demonstrated the theorem for the first time, the Green’s theorem relates the line integral along a closed line in a particular plane of a loop with the double integral under the region limited by such curve.

Let C be a simple closed curve with a defined derivative and D a region in the plane delimited by C. Let P and Q be two functions with real variables where there exists continuous partial derivatives in a region containing D. Thus,

$$\int_{A_k} \left(\frac{\partial F}{\partial x} - \frac{\partial G}{\partial y}\right) dS = \oint_{C_k} G dx + F dy \tag{4.3}$$

Where $k \in \{1,2\}$ and C_k is the portion of C that encloses A_k.

This relation is then used to calculate the area of the closed loop found in simulations. For a pinched hysteresis loop, two lobe areas are found, so the total area can then be calculated by adding the two areas from the two different lobes, by choosing F and G in a suitable way and expressing C parametrically as depicted in the figure and the following formulas:

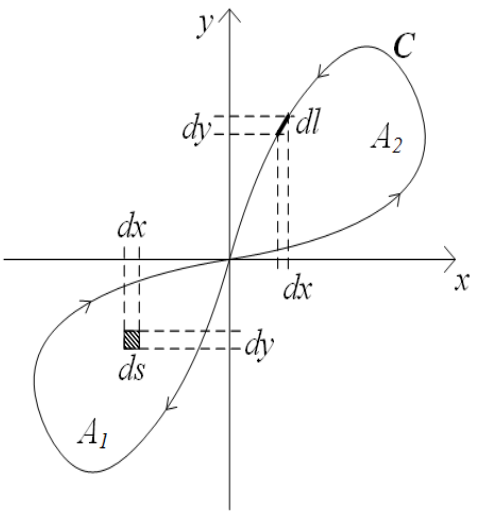


Figure 8 Green's algorithm(Capela,2013)

Once F and G need to be defined in such a way to make the integrand of the left side of (4.3) be equal to 1, $F(x,y) = 0$ and $G(x,y) = -y$ are chosen, leading to

$$\iint_{A_k} dS = \oint_{C_k} -y \,.\, dx \tag{4.4}$$

$$A_k = -\oint_{C_k} y. dx \tag{4.5}$$

$$A_k(\omega) = \int_{(k-1)\frac{T}{2}}^{k\frac{T}{2}} \left[y\frac{dy}{dt}\right].dt \tag{4.6}$$

The total area is then

$$A(\omega) = |A_1(\omega)| + |A_2(\omega)| \tag{4.7}$$

For an elliptic hysteresis loop, it is clear that there exists only a single area value, thus formulae (4.6) and (4.7) is used considering a unique value:

$$A_k(\omega) = \int_0^{kT} \left[y\frac{dy}{dt}\right].dt \tag{4.8}$$

$$A(\omega) = |A_1(\omega)| \tag{4.9}$$

4.4. Mathematical Models of Memcapacitors Used

In this section the three mathematical models of memcapacitors are described.

4.4.1. First Model: Theoretical Proposed Model Type I

The first studied and simulated model is the one proposed by the author's adviser. Such model is based in the Strukov and Williams model of the memristor, the first to be physically implement, by the HP Labs in 2008.

Once the memristor has an R_{on} and R_{off} resistance, representing the doped and undoped region, respectively, this model of memcapacitor follows the same logic by implementing an C_{on} and C_{off} memcapacitance, where, if there exists aphysical memcapacitive device, C_{on} would represent a fully doped portion of the device, whereas C_{off} would represent a state with higher impedance. These regions would vary in length according to the applied voltage at the memcapacitor's terminals.

X is a state variable representing the proportion these two halves move inside the device.

In this sense, this model is non-linear, once it takes into account the non-linearity of the dopants from the material it is made of. To take this fact into consideration, a window function is introduced in order to confine the state variable within its physical bounds. It is thus a well-behaved model where there is a well-defined equation describing the memristance of the device.

Here, the equation of the memcapacitance is explicited, and the state equation is derived from the equation that relates charge with voltage, adding however a window function, necessary for the device to operate within linear bounds.

The model is then derived the following way: From the definition of the traditional capacitor:

$$i = C\frac{dv}{dt} \tag{4.10}$$

Integrating equation (4.33) and assuming a variable memory capacitance, yields

$$q = CV \tag{4.11}$$

$$q = C_M V \tag{4.12}$$

Where

$$C_M(x) = C_{off} - (C_{OFF} - C_{ON})x \tag{4.13}$$

Is the memcapacitance of the system.

The state equation of this model can then be depicted as follows:

Let

$$\frac{dx}{dt} = kv(t)F(x) \tag{4.14}$$

Where $F(x)$ is a chosen window function, v(t) is the voltage across the memcapacitor and k is a constant related to the physical characteristics of the device.

4.4.2. Second Model: Elastic Memcapacitive System Type II

This model of memcapacitor is an example of elastic memcapacitive system and uses differential equations to describe a bistable non-volative parallel-plate memcapacitor using a strained elastic membrane to emulate its plates. The applied voltage dictates the behavior of the system, both by varying its capacitance in high and low values and by reliably switching the memcapacitor into the desired capacitance state, by setting an appropriate amplitude value. This model was studied from the article “Bistable non-volatile elastic membrane memcapacitor exhibiting chaotic behavior”(Martinez-rincon & Pershin, n.d.)

Here, the capacitor is formed by a strained membrane in the upper plate and a flat fixed lower plate. The different values of capacitance are acquired by bending the membrane up or down, allowing thus two equilibrium positions: when the membrane is in the position closer to the bottom plate, the capacitance of the device is logically defined as “1”, higher than the opposite situation, when the capacitance has a lower value and is logically defined as “0”. Both states are stable and provide a good non-volatile information storage capability (Martinez-rincon & Pershin, n.d.).

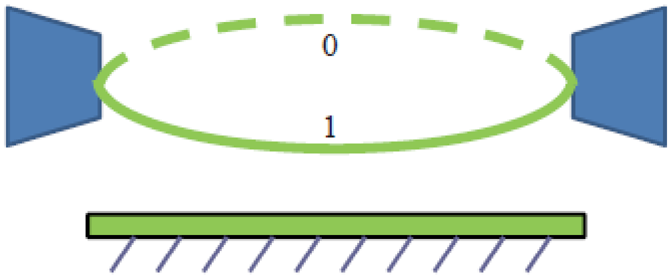


Figure 9 Elastic Memcapacitive System (Martinez-rincon & Pershin, n.d.)

There is an attractive electrostatic interaction between the charges on the fixed plate and membrane, denoted by the electric field E given by

$$E = \frac{-q}{2\varepsilon_o S} \tag{4.15}$$

Where ε_o is the vacuum permittivity and S is the area of the fixed plate.

The relation between charge and voltage is

$$q(t) = \frac{C_0}{1 + y(t)} v(t) \tag{4.16}$$

$$q(t) = C(y(t))v(t) \tag{4.17}$$

Where $y = \frac{z}{d}$ is a dimensionless variable, constituted by the separation d between the bottom plate and the middle position of the membrane and the effective displacement of the membrane from its middle non-strained position z.

A.nd the membrane’s equation of motion is

$$\frac{d\dot{y}}{d\tau} = -4\pi^2 y \left(\frac{y^2}{y_o^2} - 1\right) - \Gamma\dot{y} - \frac{\beta^2(\tau)}{(1+y)^2} \tag{4.18}$$

Where its time derivatives are taken with respect to the dimensionless time $\tau = \frac{t\omega_o}{2\pi}$ and

$$C_o = \frac{\varepsilon_o S}{d} \tag{4.19}$$

Is the initial capacitance value;

$$y_o = \frac{z_o}{d} \tag{4.20}$$

Being $\pm z_0$ the equilibrium positions of the membrane;

$$\Gamma = \frac{2\pi\gamma}{\omega_o} \tag{4.21}$$

Being γ the damping constant and ω_o the natural angular frequency of the system;

$$\beta(t) = \left(\frac{2\pi}{\omega_o d}\right)\sqrt{\frac{C_o}{2m}}v(t) \tag{4.22}$$

Where m is the mass of the membrane.

From the state equations above, once equations (4.16) and (4.18) are particular forms of equations (3.3) and (3.4), this membrane memcapacitor model is a second-order voltage-controlled memcapacitive system.

Certain range of parameters result in chaotic behavior regime and should be avoided.

4.4.3. Third Model: Superlattice Memcapacitive System Type II

The last model considered for a comparative analysis is the one exposed in the scientific article called “Solid-state Memcapacitor”. It consists on a model of a solid-state polarization-based memcapacitive device based on the slow polarization of a medium between a regular capacitor plates, derived specific through tunneling, consisting of metal layers embedded into a parallel-plate capacitor. The key idea is to use non-linear electron transport, or tunneling, for fast writing and long storage capabilities.

The operation of the memcapacitor relies on the redistribution of the internal charges Q_k between the embedded layers caused by the electric field due to the charge q on the capacitor plates. Polarization of the metamaterial results in an internal electric field due to the plate charges. Therefore, for a given amount of plate charge, the internal charges tend to decrease the plate voltage or, equivalently, to increase the capacitance.

This realization configures the capacitor constructed in internal metal layers that, along with the insulator material, form a “metamaterial” characterized by a long polarization/depolarization time. By applying an external voltage source to the capacitor, a charge redistribution between the metal layers occurs. The tunneling current between the layers depend almost exponentially on this voltage, which is important when the operation of the device is considered, allowing the writing of the information on the form of medium polarization with high-voltage pulses, and the holding of such information when low or zero voltages are applied. Once the internal metal layers and the capacitor plates are separated by an insulating material, no electron exchange between the external plates and those embedded occurs, so the tunneling occurs only between the internal metallic layers. Consequently, the total internal charge is always zero.

This feature is important for the operation of the suggested system once it allows the "writing" of information with high-voltage pulses, in the form of medium polarization, and "holding" such information when low or even zero values of voltages are applied.

The resulting memcapacitor exhibits hysteretic charge-voltage and capacitance-voltage curves, and both negative and diverging capacitance within certain ranges of the field.

a) *General N-Layers Model*

The model begins with the assumption that there exists N metal layers embedded into an insulating material of thickness δ between external capacitor plates. The structure is designed in such a way that the insulating material in between the embedded metal layers is the same as those from a regular capacitor, and the electron transport between external plates and internal layers is not possible. Therefore, the internal charges Q_k can only be redistributed between the internal layers creating a medium polarization.

The following figure draws the schematics of such model, with its charge state variables and other physical parameters.

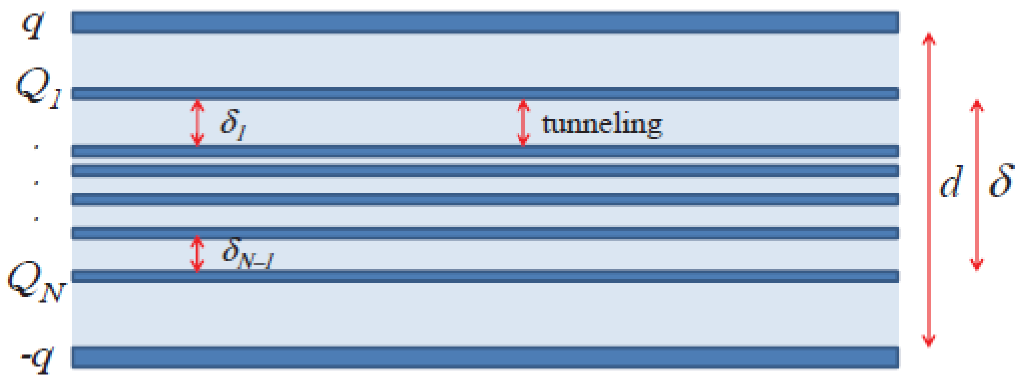


Figure 10 Solid-state general layers (Martinez, DiVentra)

Correspondingly, there is a constrain imposed on the total internal charge:

$$\sum_{k=1}^{N} Q_k(t) = 0 \tag{4.23}$$

That means, the total internal charge is always zero, once the operation of the device relies on the redistribution of the internal charges between the layers caused by the electric field due to the charge on the capacitor plates. Polarization of the metamaterial results in an internal electric field between the layers opposite to the electric field generated by the plate charges. As a consequence, the internal charges tend to decrease the plate voltage and increase the capacitance.

The capacitance of the total structure is given by

$$C = \frac{q}{V_C} = \frac{2C_0}{2 + \sum_{i=1}^{N} [\Delta - 2\Delta_{i-1}] \frac{Q_i}{q}} \tag{4.24}$$

Where

$$\Delta = \frac{\delta}{d} \tag{4.25}$$

$$\Delta_i = \sum_{j=1}^{i} \frac{\delta_j}{d} \; for\; i = 1,2, \dots, N-1 \tag{4.26}$$

$$\Delta_0 = 0 \tag{4.27}$$

$$C_0 = \frac{\varepsilon_0 \varepsilon_r S}{d} \tag{4.28}$$

Are geometry-related parameters: C_0 is the capacitance of the system when no internal metal layers are considered; V_C is the external plate voltage, defined as

$$V_C = 2dE_q + \delta E_1 + [\delta - 2\delta_1]E_2 + [\delta - 2(\delta_1 + \delta_2)]E_3 + \cdots + [\delta - 2(\delta_1 + \cdots + \delta_{k-1})]E_k \dots - \delta E_N \tag{4.29}$$

Where

$$E_q = \frac{q}{2S\varepsilon_0 \varepsilon_r} \tag{4.30}$$

Is the magnitude of the uniform electric field due to the charge q ate the external plate in the direction perpendicular to the plane, where ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant of the insulating material and S is the area of the plates.

$$E_k = \frac{Q_k}{2S\varepsilon_0 \varepsilon_r} \tag{4.31}$$

Is the electrical field due to the charge Q_k at the k-th embedded metal layer. For the sake of simplicity, equation (4.17) can be rewritten as:

$$V_C = \frac{q}{C_0}\left[1 + \Delta\frac{Q_1}{2q} + (\Delta - 2\Delta_1)\frac{Q_2}{2q} + \cdots + (\Delta - 2\Delta_{k-1})\frac{Q_k}{2q} \ldots - \Delta\frac{Q_N}{2q}\right] \qquad (4.32)$$

Which makes more sense when analyzing equation (4.12).

Equation (4.12) explicits diverging values of capacitance when its denominator assumes the value of zero, while its numerator reaches a finite number. Negative and diverging values of capacitance have been found experimentally in ionic memcapacitors, for instance, in nanopore membranes in an ionic solution subject to external time-dependent perturbations.

Physically, it can be explained when the internal metal layers completely screen the external field, despite the presence of a finite charge q on the external capacitor plates. This explains the physical phenomenon of diverging values of capacitance. At certain instants of time, the internal metal layers may over-screen the external field, resulting in a negative capacitance, which is experimentally observed in different solid-state systems, but not accompanied by hysteretic and diverging values of capacitance.

For the description of the dynamics of the internal charges Q_k in the system, the voltage V_k is defined as the voltage between k and k+1 metal layers as depicted in equation (4.33)

$$V_k = -E_{k,k+1}\delta_k \qquad (4.33)$$

Where the electrical field between two neighboring layers $E_{k,k+1}$ is obtained adding the electric fields due to charges – that means, equation (4.13) – at all layers and the external metal plates – in equation (4.12), in such a way that

$$E_{k,k+1} = -2E_q - E_1 - E_2 \ldots - E_k + E_{k+1} + E_N \qquad (4.34)$$

$$E_{k,k+1} = \frac{-2q - (Q_1 + \cdots + Q_k) + (Q_{k+1} + \cdots + Q_N)}{2S\varepsilon_0\varepsilon_r} \qquad (4.35)$$

The dynamics of the charge at a metal layer k is determined by the currents flowing to and from that layer:

$$\frac{dQ_k}{dt} = I_{k-1,k} - I_{k,k+1} \qquad (4.36)$$

Where $I_{k,k+1}$ is the tunneling electron current flowing from layer k to layer k+1, defined by

$$I_{k,k+1} = \frac{Se}{2\pi h\delta_k^2}\left[\left(U - \frac{eV_k}{2}\right) exp\left[-\frac{4\pi\delta_k\sqrt{2m}}{h}\sqrt{U - \frac{eV_k}{2}}\right] - \left(U + \frac{eV_k}{2}\right) exp\left[-\frac{4\pi\delta_k\sqrt{2m}}{h}\sqrt{U + \frac{eV_k}{2}}\right]\right] \quad (4.37)$$

If $eV_k < U$
And

$$I_{k,k+1} = \frac{Se^3V_k^2}{4\pi hU\delta_k^2}\left[exp\left[-\frac{4\pi\delta_k\sqrt{m}U^{3/2}}{ehV_k}\right] - \left(1 + \frac{2eV_k}{U}\right) exp\left[-\frac{4\pi\delta_k\sqrt{m}U^{3/2}}{ehV_k}\sqrt{1 + \frac{2eV_k}{U}}\right]\right] \quad (4.38)$$

Equation (4.24) is the state equation of this charge-controlled memcapacitive system, once the layer charges Q_k are considered state variables of the equation.

This memcapacitor, when in series with an ac voltage source, models the following differential equation of the charge inside the device, which, according to the definition of the memory devices already explained, is itself a state variable:

$$v(t) = R\frac{dq}{dt} + \frac{q}{C} \quad (4.39)$$

b) Two-Layers Memcapacitive System

The simplest system derived from the previous general model exhibiting polarization memory is a two-layer memcapacitor.

Beginning at $q = 0$, the applied sinusoidal voltage induces electron tunneling between the internal metal layers resulting in a non-zero Q_1 andQ_2. Positive half periods of v induce negative Q_1 and positive Q_2 charges, andy cause a screening electrical field opposite to the electric field of plate charges.

The following figure exemplifies the physical schematics of this approximation when N=2.

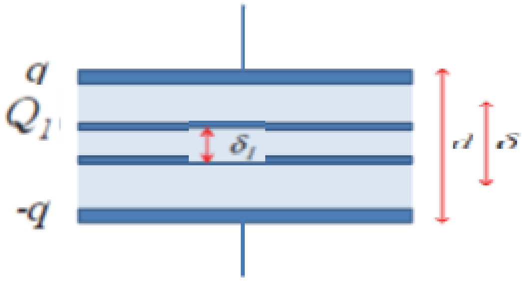


Figure 11 Solid State Memcapacitor for k=2 (Martinez, DiVentra)

The equations for the two-layers model can thus be derived from the general model, and written as follows:

For k=2, equation (4.5) leads to

$$\sum_{k=1}^{2} Q_k(t) = 0 \implies Q_1 + Q_2 = 0 \tag{4.40}$$

This definition yields the important relation, which will dictate the form of the subsequent equations:

$$Q_2 = -Q_1 \tag{4.41}$$

For N=2,

$$\delta = \delta_1 \; and \; \Delta = \Delta_1 \tag{4.42}$$

Where

$$\Delta = \Delta_1 = \frac{\delta_1}{d} = \frac{\delta}{d} \tag{4.43}$$

When equations (4.12) and (4.13) assume the particular cases for k=2

$$E_1 = \frac{Q_1}{2S\varepsilon_0\varepsilon_r} \tag{4.44}$$

$$E_2 = \frac{Q_2}{2S\varepsilon_0\varepsilon_r} \tag{4.45}$$

Equation (4.28), the voltage in the model assumes the form

$$V_c = \frac{q + \Delta Q_1}{C_0} \tag{4.46}$$

From equations (4.16) and (4.17), the first two terms of the electric field takes the form

$$E_{1,2} = -2E_q - E_1 - E_2 \tag{4.47}$$

$$E_{1,2} = \frac{-(q + Q_1)}{S\varepsilon_0\varepsilon_r} \tag{4.48}$$

The capacitance of the whole structure is thus defined as

$$C = \frac{qC_o}{q + \Delta Q_1} \tag{4.49}$$

The system's state equation can then be depicted in the form of the two equations that describe the charge dynamic of the system:

$$\frac{dQ_1}{dt} = -I_{1,2} \tag{4.50}$$

$$\frac{dQ_2}{dt} = I_{1,2} \tag{4.51}$$

Where the currents associated in equations (4.50) and (4.51) are defined as a particular case of equation (4.38), as follows:

$$I_{1,2} = \frac{Se}{2\pi h\delta_1^2}\left[\left(U - \frac{eV_1}{2}\right) exp\left[\frac{-4\pi\delta_1\sqrt{2m}}{h}\sqrt{U - \frac{eV_1}{2}}\right] - \left(U + \frac{eV_1}{2}\right) exp\left[\frac{-4\pi\delta_1\sqrt{2m}}{h}\sqrt{U + \frac{eV_1}{2}}\right]\right] \tag{4.52}$$

If $eV_1 < U$, and

$$I_{1,2} = \frac{Se^3V_1^2}{4\pi hU\delta_1^2}\left[exp\left[\frac{-4\pi\delta_1\sqrt{m}U^{3/2}}{ehV_1}\right] - \left(1+\frac{2eV_1}{U}\right)exp\left[\frac{-4\pi\delta_1\sqrt{m}U^{3/2}}{ehV_1}\sqrt{\left(1+\frac{2eV_1}{U}\right)}\right]\right] \tag{4.53}$$

If $eV_1 > U$

From the charge equation (4.39), a manipulation of equation (4.49) to explicit the initial capacitance C_o and the definition of the current as the first derivation of the charge, the charge in a two-layer memcapacitive system is thus defined as:

$$\dot{q} = \frac{vC_o - q + \Delta Q_1}{RC_o} \tag{4.54}$$

$$q = \Delta Q_1 + vC_o - iRC_o \tag{4.55}$$

Equation (4.40) then takes the form

$$I_{1,2} = \left[A_-(q,Q_1)e^{EX1_-(q,Q_1)} - (q,Q_1)e^{EX1_+(q,Q_1)}\right] \tag{4.56}$$

By making

$$A_-(q,Q_1) = \frac{2e_qUS\varepsilon_0\varepsilon_r - e_q^2\delta_1(q+Q_1)}{4\pi h\delta_1^2\varepsilon_0\varepsilon_r} \tag{4.57}$$

$$A_+(q,Q_1) = \frac{2e_qUS\varepsilon_0\varepsilon_r + e_q^2\delta_1(q+Q_1)}{4\pi h\delta_1^2\varepsilon_0\varepsilon_r} \tag{4.58}$$

$$EX1_-(q,Q_1) = -\frac{4\pi\delta_1\sqrt{2m}}{h}\sqrt{\left(\frac{2US\varepsilon_0\varepsilon_r - e\delta_1(q+Q_1)}{2S\varepsilon_0\varepsilon_r}\right)} \tag{4.59}$$

$$EX1_+(q,Q_1) = -\frac{4\pi\delta_1\sqrt{2m}}{h}\sqrt{\left(\frac{2US\varepsilon_0\varepsilon_r + e\delta_1(q+Q_1)}{2S\varepsilon_0\varepsilon_r}\right)} \tag{4.60}$$

The same steps are made for equation (4.41):

$$I_{1,2} = L(q,Q_1)\left[e^{EXP_3(q,Q_1)} - M(q,Q_1)e^{EXP_3(q,Q_1)\sqrt{M(q,Q_1)}}\right] \tag{4.61}$$

Where

$$L(q,Q_1)=\frac{{e_q}^3(q+Q_1)^2}{4\pi hUS\varepsilon_o^2\varepsilon_r^2} \tag{4.62}$$

$$EXP_3(q,Q_1)=-\frac{4\pi S\varepsilon_0\varepsilon_r\sqrt{m}U^{\frac{3}{2}}}{e_q h(q+Q_1)} \tag{4.63}$$

$$M(q,Q_1)=\frac{US\varepsilon_0\varepsilon_r+2e_q\delta_1(q+Q_1)}{US\varepsilon_0\varepsilon_r} \tag{4.64}$$

The added and removed energy to and from the capacitor is defined as equation (4.65):

$$U_C=\int_0^t V_C(\tau)i(\tau)d\tau \tag{4.65}$$

Which indicates that the present model operates as a dissipative system, once the amount of added energy is on average larger than the amount of removed energy, resulting thus in positive values of (4.65). Such process can be explained by the dissipation of energy caused by thermalization processes due to the different electromechanical potential energies of each metal layers which accompanies the tunneling between internal layers, as well as local heating expected in real devices.

Next chapter defines the values used in simulations and the results achieved for each model here presented.

Chapter Five: Parameters used and Simulations Results

Here, a brief description of the parameters used in the simulations of the systems, as well as an explanation of the codes used and the results obtained.

5.1. Description of the model parameters

a) First Model: Theoretical Proposed Model

The first model was initially simulated using the Matlab script called Memdevice_view.m. This piece of code aims to solve the differential equation which describes the state variable *x* described by equation (4.14) using the Matlab function *ode15s*; after obtaining the values of *x*, equation (4.12) was used to calculate the charge that passes through the system.

The parameters used were:

$$C_{on} = 10pF$$

$$C_{off} = 1nF$$

The value of C_{off} is much higher than C_{on}, following the assumption of $R_{off} \gg R_{on}$ in the memristor's theory, in order to perform the on switching of the device.

For the Prodromakis window function, the parameters used were:

$A = 1$, for the amplitude of the window, and $p = 5$, for the control parameter.

$k = 1000$ is a process parameter that takes into account the physical characteristics of the device.

Using the angular frequency $\omega = 2\pi f$, plots of $q(t), v(t)$ in function of time were generated; the hysteresis plot $q - v$ revealed a type I pinched hysteresis loop: once $q(0) = 0$ for $v(0) = 0$, the plot passes through the origin of the axis, creating thus two lobes in the odd quadrants of the plane, showing positive and negative values. This Lissajous figure is a direct consequence of the periodic nature of the variables *q* and *v*, subjected to the same frequency.

The symmetrical hysteretic curve is very similar to the one found in memristors, and thus it is considered to be a well-behaved model. It thus can serve as a model from which the other memcapacitors can be compared, in a measure of how much they are far from the ideal model.

The critical frequency is the initial value of frequency from which the *q*-*v* graph begins to show a pinched hysteretic behavior. Here, after successive iterations it was discovered that the critical frequency for that model is around f=50Hz.

The hysteresis plot of capacitance versus input voltage shows a circular hysteresis loop, clearly falling into type II classification mark, once the graph does not pass through the origin.

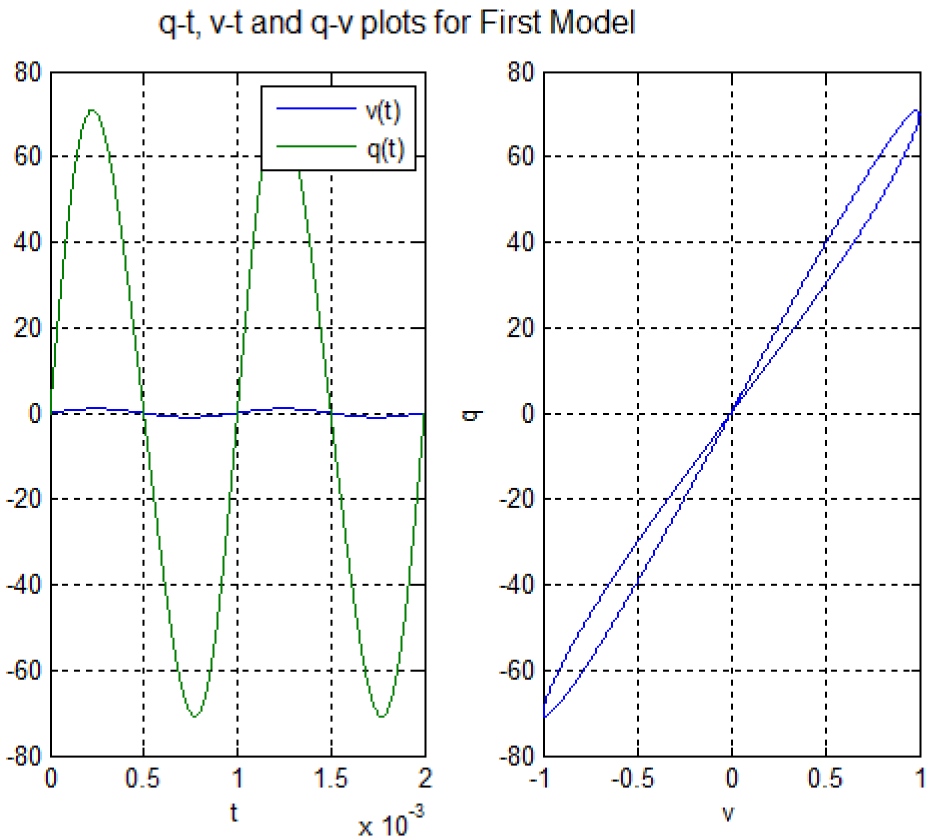


Figure 12 q-t and v-t plot and q-v Hysteresis plot for Type I Theoretical Model

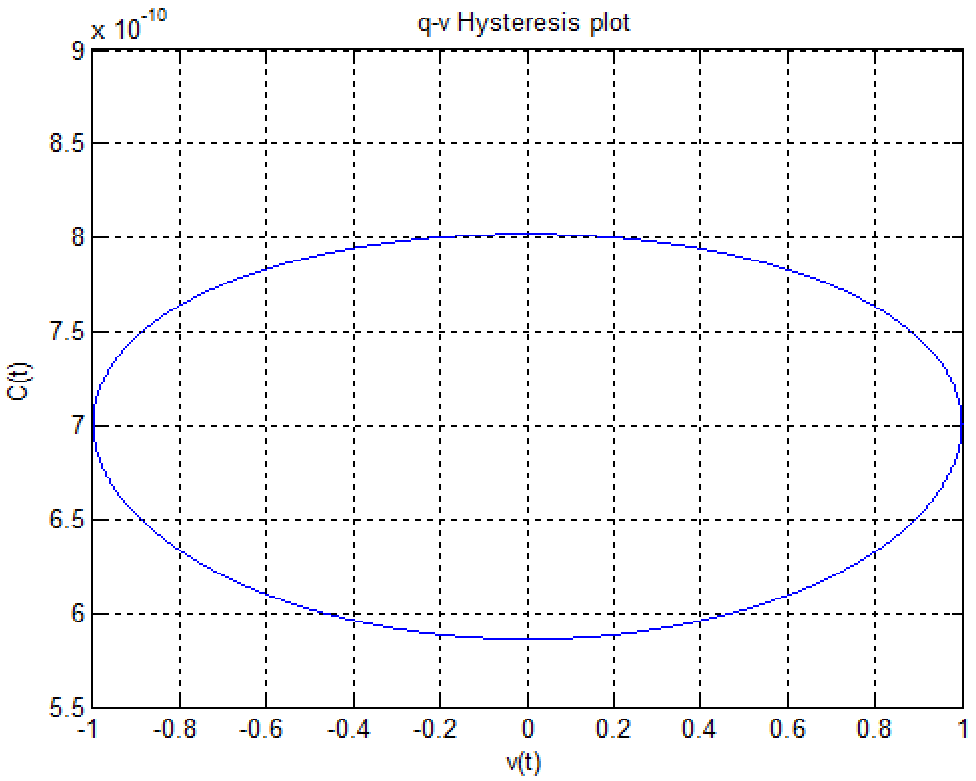


Figure 13 q-v Hysteresis plot for First Model

Another method for amplitude and frequency characterization of the models consists of taking a morphological measure of the area of the lobes against amplitude or frequency dependence characterization of memcapacitors.

The proposed approach analyses the area of the associated hysteresis loop with a sweep of amplitude and frequency values of the input voltage, in order to check the behavior of the systems to a different set of amplitudes and frequencies, having an easier scale to interpret the results.

A script called “Memdevice_area.m” performs the calculations of the areas of the two lobes from the hysteresis plot, by varying the input frequencies, and plot the results in db.

The graph was coded first by defining a row vector of logarithmically spaced values of size N=100001 elements:

```
wspace=logspace(1,5,N);
```

For N iterations, the angular frequency is thus defined as a vector of values

```
w=wspace(n);
```

And the areas is then calculated, using only the first period of the sinusoid

```
Area(n)=abs(q(:,1:(Ns+3)/4)*dv(:,1:(Ns+3)/4)')+abs(q(:,(Ns+3)/4:end)*dv(:,(Ns+3)/4
:end)');
```

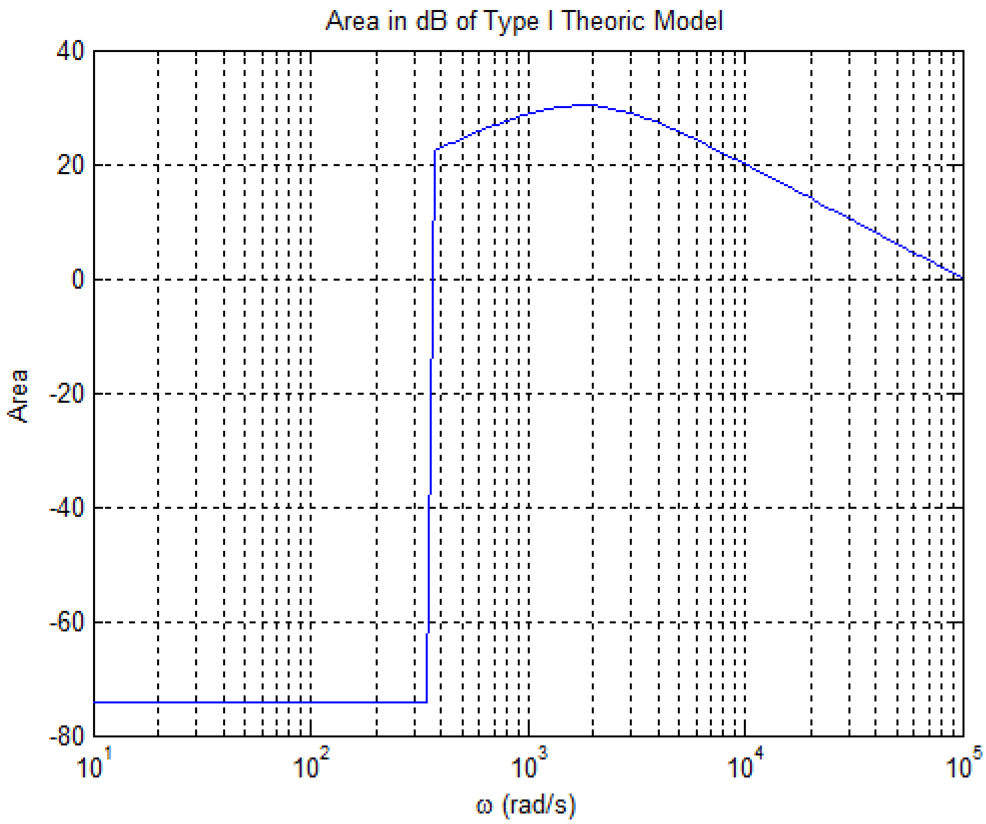


Figure 14 Area of Type I Memcapacitor Model for a frequency sweep

The same logic was used to plot the amplitude variations of the model against the area of the loop, with slight changes: a row vector of logarithmically spaced values of size N=100001 elements was created, then, inside the iteration loop, a vector of v_0 values was formed:

vspace=logspace(0,1,N);

vo=vspace(n);

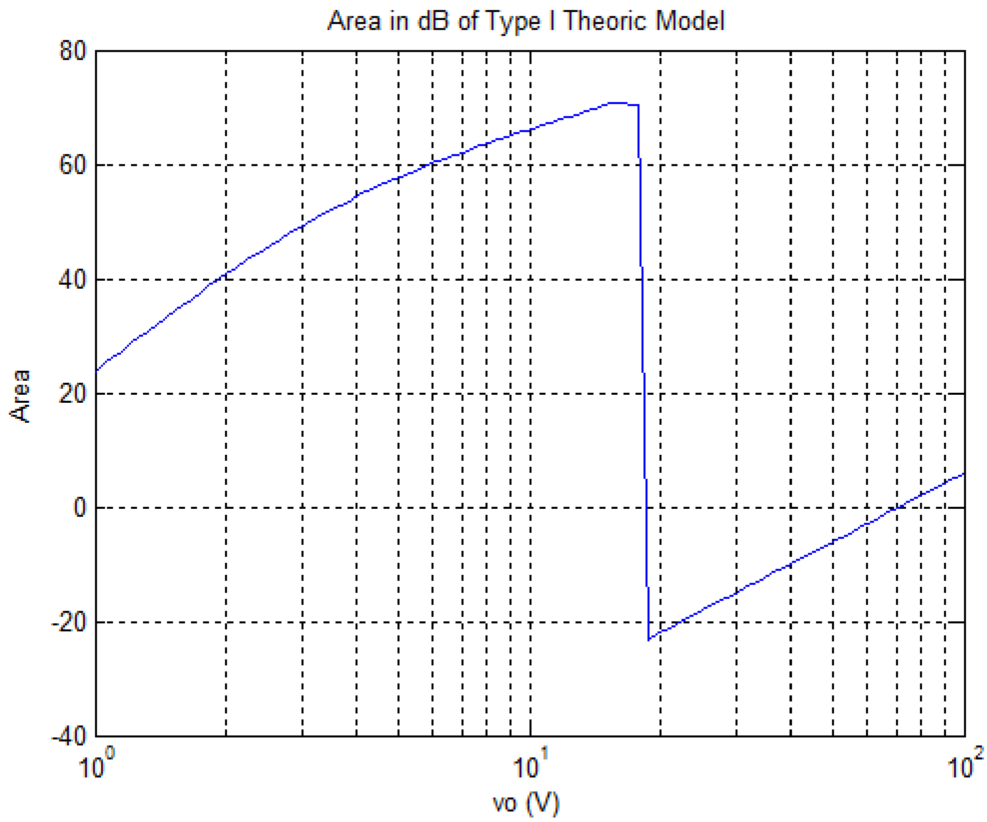


Figure 15 Area of Type I Memcapacitor model for amplitude sweep

b) Second Model: Elastic Memcapacitive System

This model was initially simulated using the Matlab script called Memdevice_view.m. This piece of code aims to solve the differential equation which describes the state variable *x* described by equation (4.18) using the Matlab function *ode15s*; after obtaining the values of the state variable, equation (4.16) was used to calculate the charge that passes through the system.

The parameters used were:

$$gamma = 0.7$$

$$beta0 = 2.7$$

$$y0 = 0.2$$

Using the angular frequency $\omega = 2\pi f$, plots of $q(t), v(t)$ in function of time were generated; the hysteresis plot $q - v$ revealed a type II pinched hysteresis loop.

The critical frequency is the initial value of frequency from which the *q-v* graph begins to show a pinched hysteretic behavior. Here, after successive iterations it was discovered that the critical frequency for that model is around f=0.5Hz

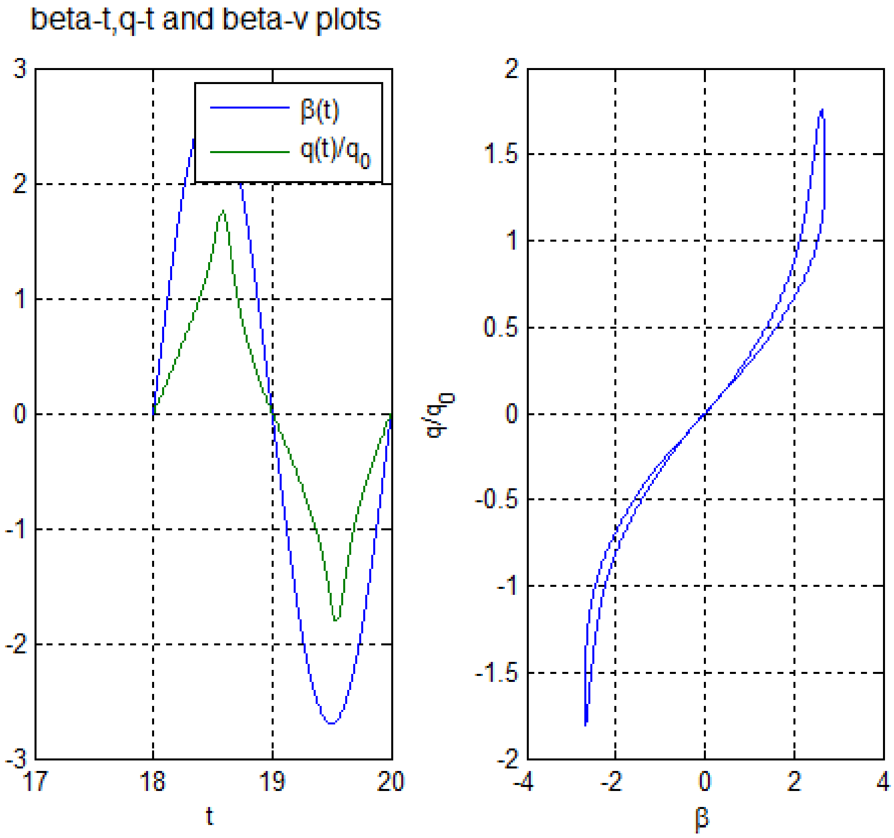


Figure 16 q-t and v-t plots and q-v hysteresis loop for Type II elastic model

The capacitance-voltage curve is plotted in figure (17). Here a slightly shift in the origin of the axis is seen, but the hysteresis curve is present, although it is a pinched one, in opposition to the elliptical hysteresis curve found in Model I.

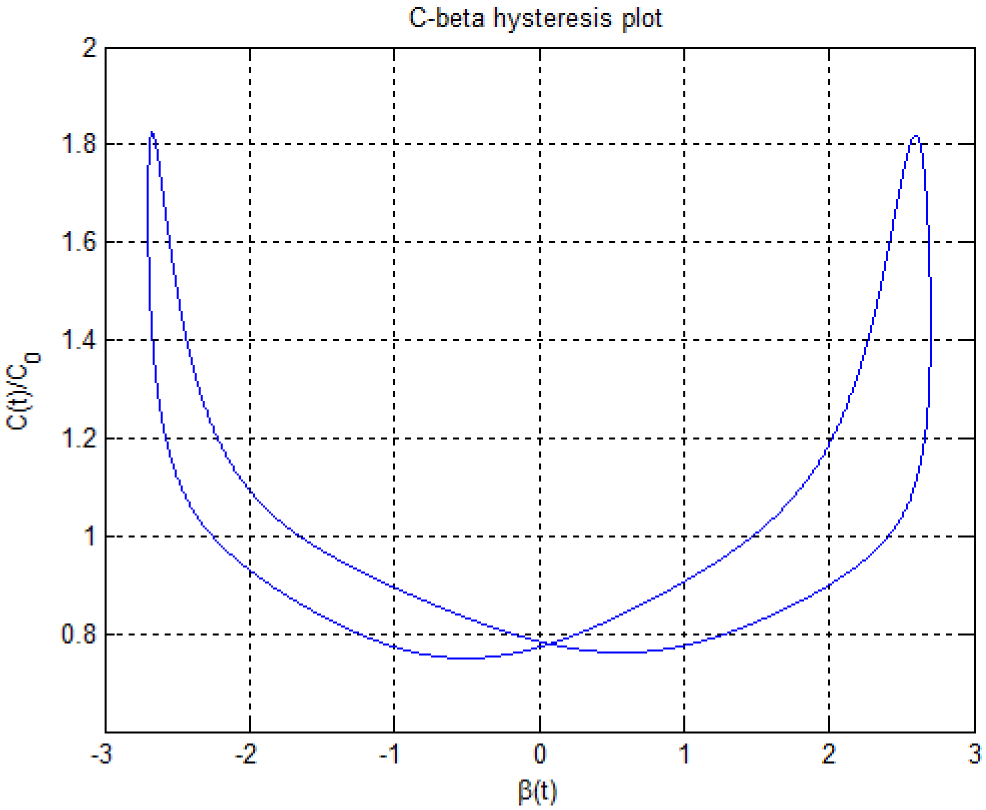


Figure 17 C-vHysteresis loop for Type II elastic Model

c) Third Model: Superlattice Memcapacitive Model

This model was initially simulated using the Matlab script called Memdevice_view.m. This piece of code aims to solve the differential state equations (4.50) and (4.51) of the system, using the Matlab function *ode15s,* by calling the function "Fmemstate.m" ; after obtaining the values of the state equation, the charge that passes through the system was calculated, as well as the charges Q_1 and Q_2 due to its internal layers.

An important feature of this model was the definition of the constants used. Once they describe physical characteristics of the system in an atomic level, they played a significant role in the success of the code compilation. Conversion of units were also problematic.

$$h = 4.1356674335 * 10^{-15}\ eVs;$$

$$h = 6.62606957 * 10^{-37}\ m^2 g/s$$

$$e = 1.60217656535 * 10^{-19}$$

$$me = 9.1093821545 * 10^{-34}\ g$$

$$\varepsilon_0 = 08.854187817 * 10^{-12}\ F/m$$

$$\varepsilon_r = 5$$

$$d = 100nm$$

$$S = 10mm^2$$

$$d_1 = 50nm$$

$$U = 0.33\ eV$$

$$R = 1\Omega$$

The function “jk.m” models the tunneling current density as a function of the voltage drop between two adjacent layers, and the associated function “testJk.m” plots its results in a logarithmic fashion, as depicted in figure (18). The specific parameter used here was $U = 0.5eV$. This graph is a direct solution from equations () and (), and clearly shows the growth of such current in function of the applied voltage.

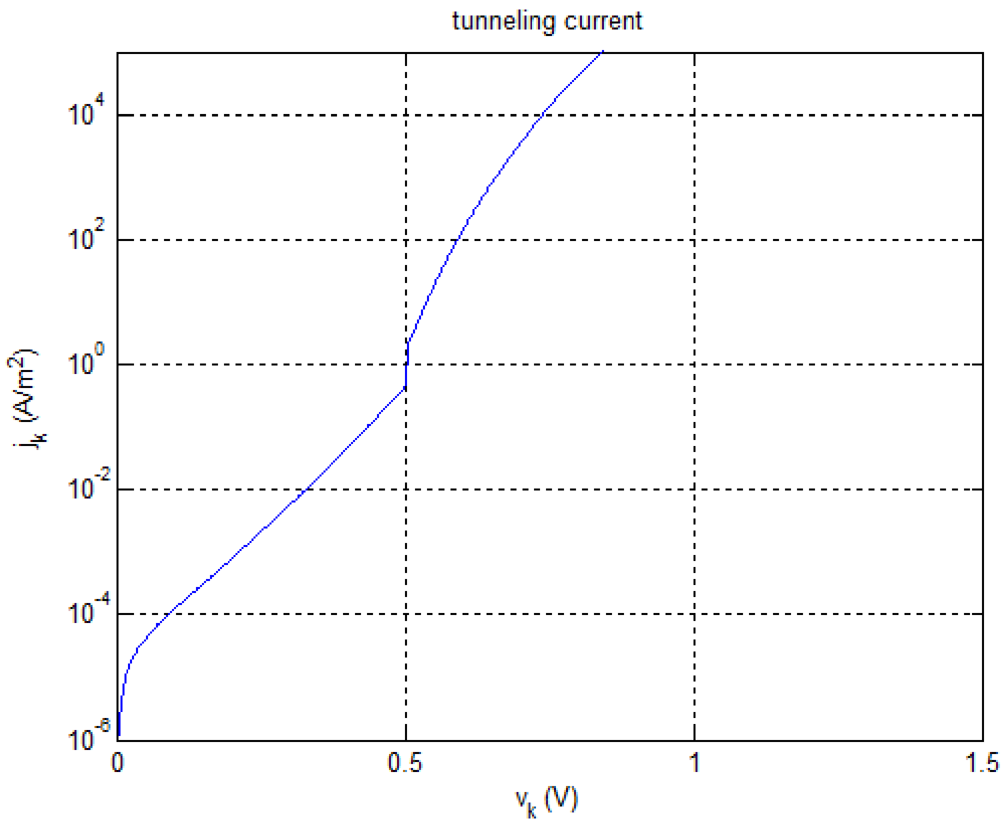


Figure 18 Tunneling current for the third model

The following plot show the values of Q_1, Q_2 and q in function of time. Once $v(0) = 0$ as $v(t) = v_o \sin(2\pi f t)$, and $Q_1(0) = Q_2(0) = 0$, the sinusoidal voltage induces electron tunneling between the internal metal layers, resulting, at the end of the simulations, in non-zero values for the charges Q_1 and Q_2. Here it is clearly shown the symmetric value of Q_2 as already predicted in equation () as well as the sinusoidal nature of the three charges involved in this model: positive half periods of the input sinusoidal voltage induce a negative Q_1 and positive Q_2. In turn, they cause a screening electric field opposite to the electric field due to the plate charges.

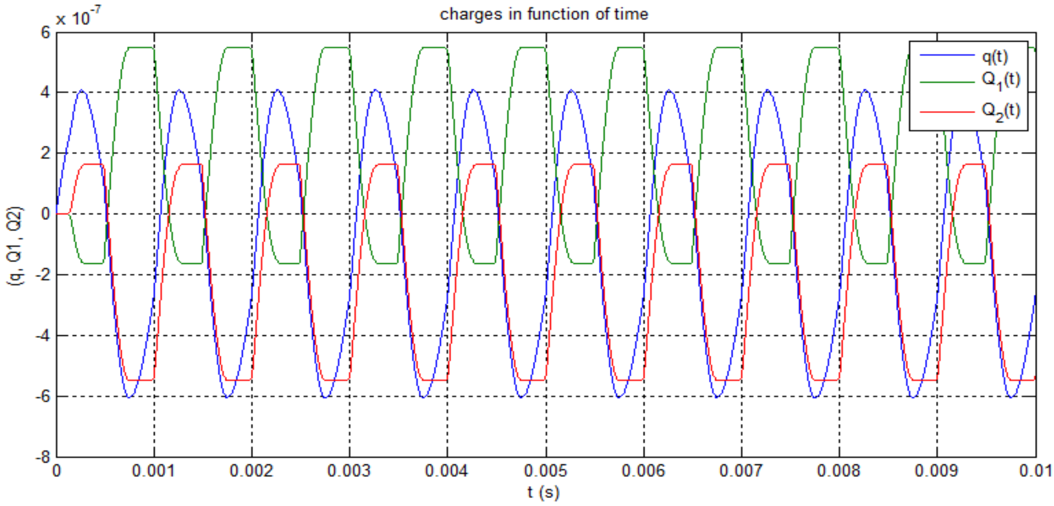


Figure 4 Charges in function of time for the third model

The most important feature of this model is the formation of a non-pinched hysteresis loop in the *q-v, Q1-v* and *Q2-v* planes. Once these planes do not cross the origin, it is suffice to say that they are classified as a type II hysteresis loop. Despite most of the memristor models and, as far as the memcapacitors models analysed in this work are concerned, exhibit a pinched hysteresis loop, this model shows an elliptical hysteresis loop, far beyond the well-behaved first model from which it is compared. A physical explanation of such phenomenon lies in the internal polarization of the memcapacitor: when the plate charge is zero, it creates a non-zero voltage drop on the structure, in such a way that, for $q = Cv$, $v_c = 0$ at $q \neq 0$. Mathematically, this condition explains why the loop does not cross the origin of the axis.

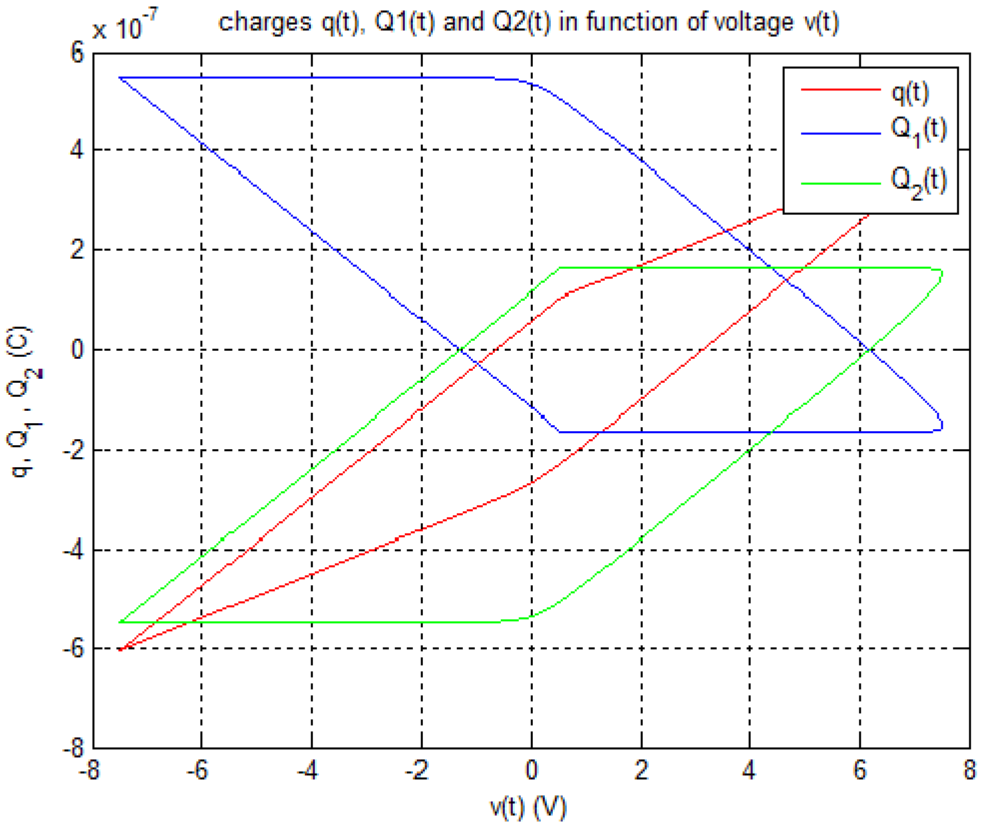


Figure 5 Hysteresis Loop of the charges involved in the Third Model

5.2. Amplitude Changes

An analytical solution of the state equations of the memcapacitor models is possible when the state variable *x*, the output variable y and the angular frequency ω are periodic functions of time under special driving stimulus conditions, as in amplitude ranges of *x*. For a small window of amplitude values, plotting y against x reveals the characteristic hysteresis loop as a manifestation of the memory property, revealing that y exhibits different values for the same value of the input x.

Hence, for the three models studied an amplitude sweep is made, in order to reach a characterization of the behavior of the model as amplitude values change in time.

a) For the first model

After several values of amplitude were tested, a range of allowed amplitudes was found, that means, a set of values where a typical pinched memcapacitance hysteresis plot can be found. For this model, in a range from 0.01 V to 1 V a type I hysteretic behavior is found, both for the *q-v* plots and for the capacitance-voltage loop, for the same value of frequency. In this case, $f = 1Hz$.

The low values of amplitude observed show that the transitions occur in a very fast mode.

For lower values of amplitude a linear dependency is found, and for higher values, the graph again shows linear behavior. That means to say that, for increasing values of the amplitude used at each iteration, the loop changes from smooth to sharp behaviors. The sharp behavior, showing the asymptotic values of C_{on} and C_{off}, is identified with hard switching conditions , occurring with the physical limits of the device approaching the boundaries.

Increasing further the amplitude of the driving signal will lead to the collapse of the hysteretic behavior. For lower amplitudes, the loop displays a smooth behavior as a result from soft switching conditions, when the physical boundaries of C_{on} approaches the boundaries. Further decreasing the amplitude leads to the total collapse of the hysteretic behavior. For these cases, the device must be in its off state.

The method of amplitude characterization also led to the identification of the critical value of amplitude. That means, the initial value of initial amplitude from which the device begins to show hysteretic effects in its *q*-*v* plane. In the present case, $v_o = 0.1V$, according to figure (21).

Figure (22) also shows the behavior of the charge across the device as a function of time. Here it is clearly seen the change from smooth sinusoidal behavior to a much degenerate sinusoid as the amplitude reaches its upper boundary, although the periodic characteristic remain present.

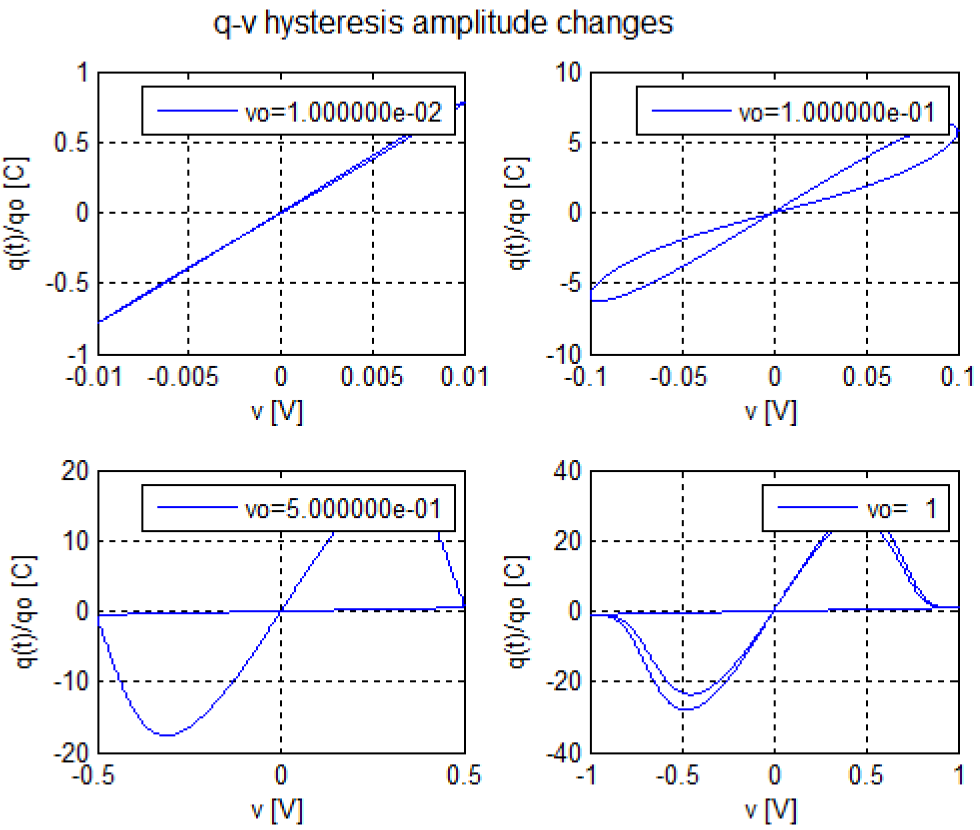


Figure 21 Hysteresis Plots for different values of amplitudes in the first model

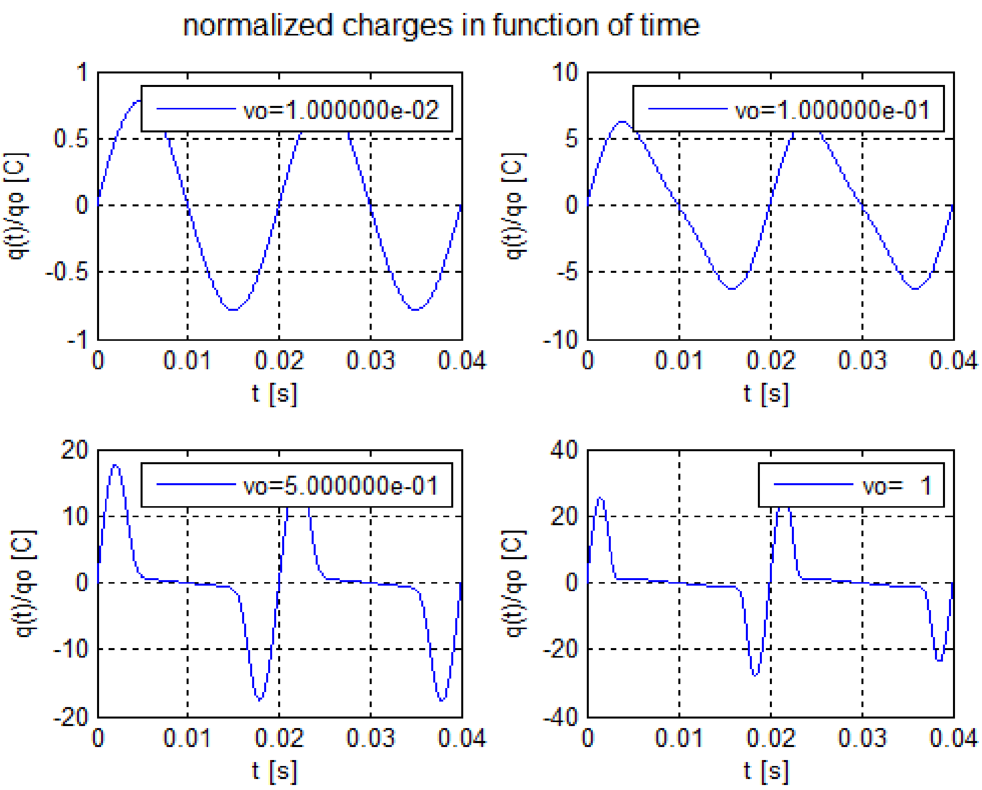


Figure 6 Normalized charge in function of time for the First Model

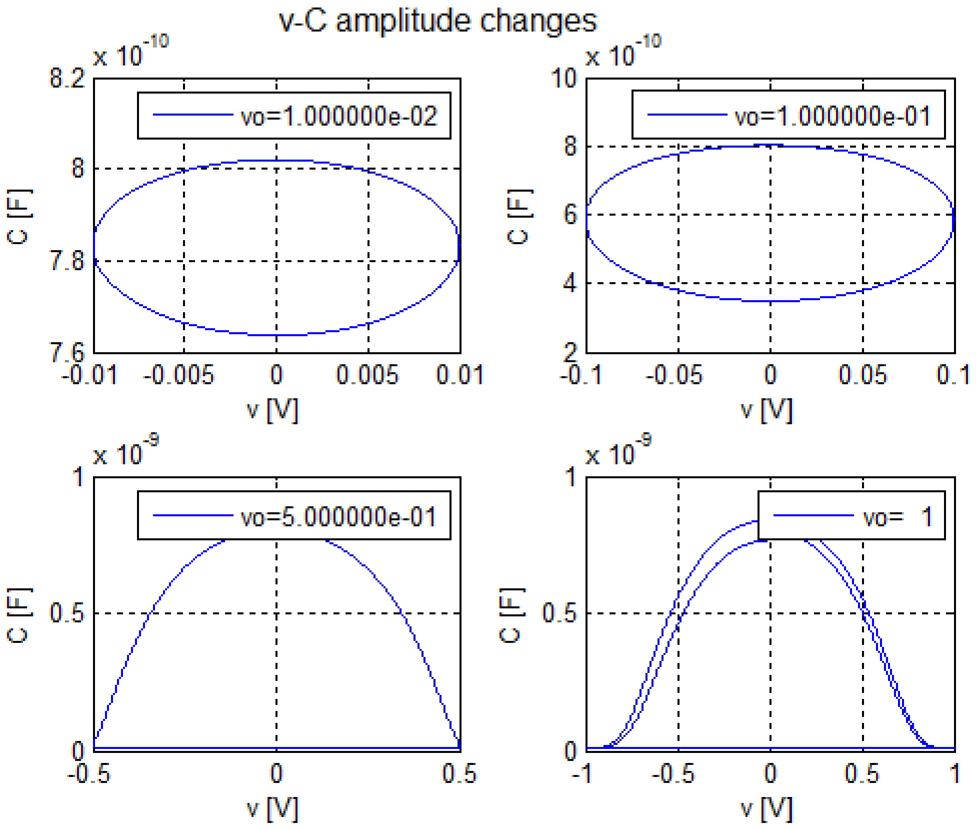


Figure 7 C-v plots for different values of amplitude for the First Model

Figure (23) shows the variation of the *C-v* hysteresis plots for different values of amplitude. Here, the particular value of $v_0 = 0.5V$ marks the abrupt change from a well-behaved hysteresis loop to a degenerated one. This value should then be taken into account when designing circuits where the change in amplitude voltage is required, once it will chage the behavior of the memcapacitor, and, thus, the circuit as a whole.

b) For the second model

β_0 is a normalized value which depends on physical factors of the system. Therefore, it is not possible to perform an amplitude sweep, and vary this parameter, once the results may turn to be impredictable and do not translate any characteristic of the system. From this observation, it can be said that the system is ergodic and does not reach a steady-state solution.

c) For the third model

After several values of amplitude were tested, it was found that the changes in amplitude for the three charges involved in this model follow the behavior of figure (3): a type II ellipsoidal hysteresis loop, where no cross on the origin of the axis is observed.

For this model, the values of amplitude capable of create a hysteretic loop are higher than the theoretical model: the range goes from $v_o = 3V$ to $v_o = 100V$, for $f = 1Hz$.

By analyzing the three charges involved, there is a clearly difference among *q* and the other two layer charges *Q_1* and *Q_2*. The area of the loop is lower for q at the same values of amplitude than the other ones, so it is safe to say that its critical amplitude is lower than for *Q_1* and *Q_2*.

For amplitude changes in *q,Q_1* and *Q_2,* the hysteresis plot degenerates into a straight line at $v_0 = 100V$, while it maintains a bigger area around $v_0 = 20V$, as depicted in figures (24), (25) and (26). Figures (25) and (26) also explicit the symmetric nature of the charges *Q_1* and *Q_2.*

Comparing those values of amplitude to the values found in the First Model, it can be seen that the third model can handle a broader range of amplitude values before degenerate into a straight line, being thus more robust to amplitude changes in a circuit.

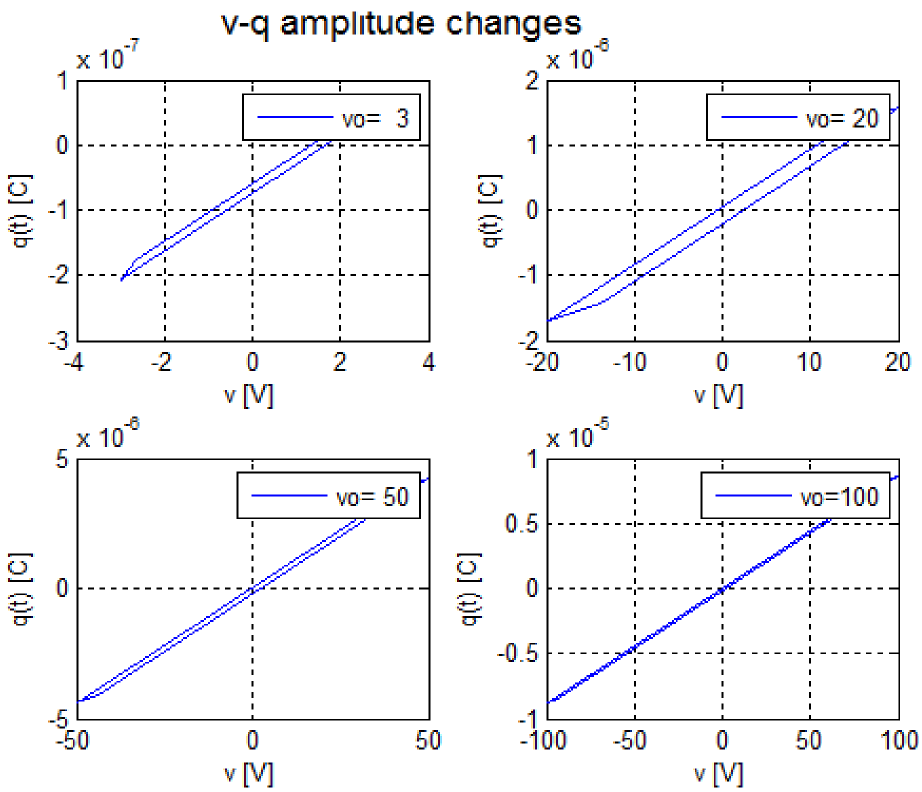


Figure 8 Hysteresis plots for q as amplitude changes

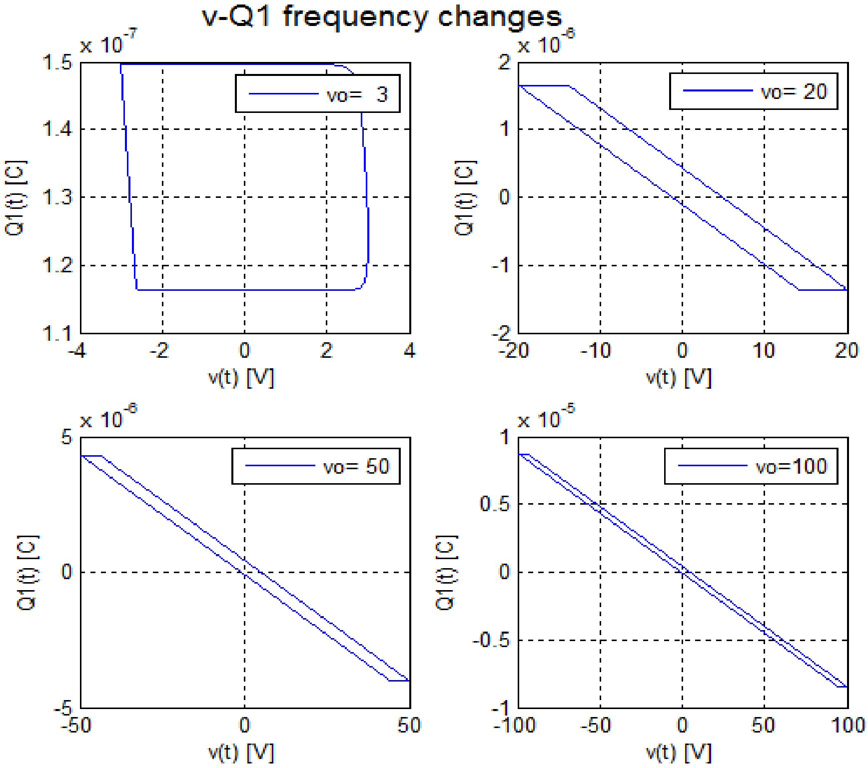


Figure 95 Hysteresis Plots for Q1 as amplitude changes

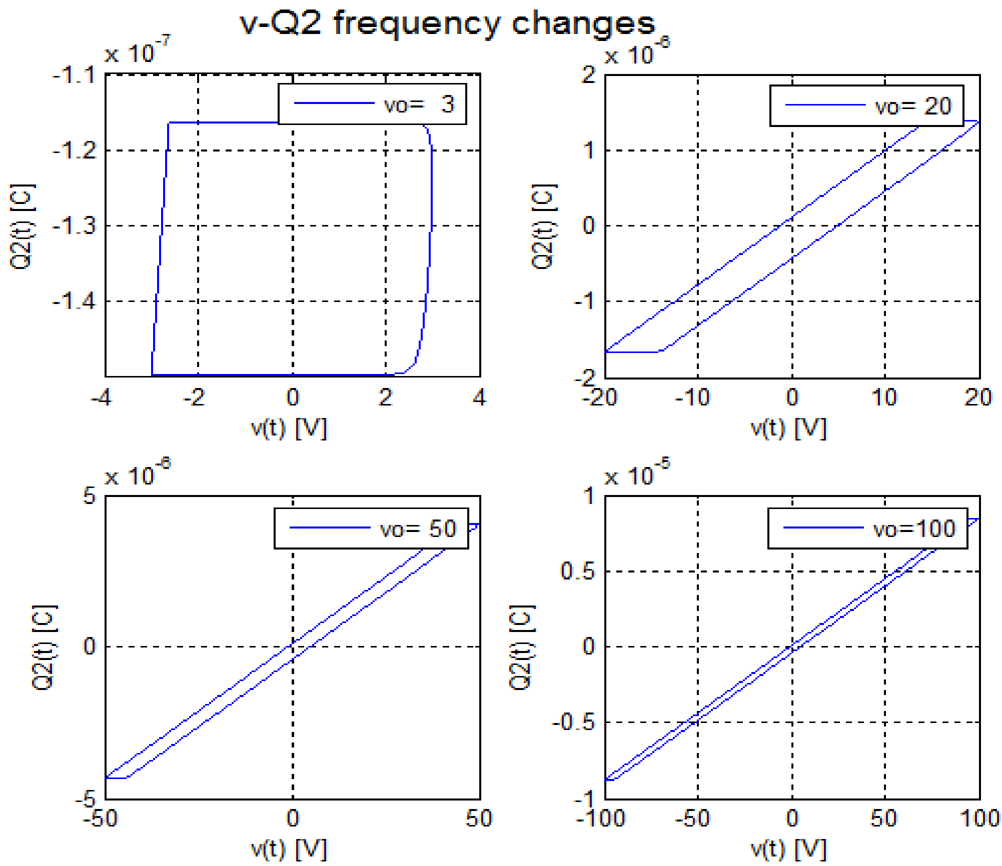


Figure 26 Hysteresis plots for Q2 as amplitude changes

5.3. Frequency Changes

Morphological based method to address the frequency dependence characterization of memcapacitors. The proposed approach analyses the area of the associated hysteresis loop, and the ability of the device to maintain non-zero area as frequency increases as figure of merit for frequency characterization, in order to harvest values of frequency from which the models studied can operate in a circuit.

a) for the first model

As it can be seen in figures (27) and (28), the area plots degenerate into a straight line as frequency rises, which is consistent with the third fingerprint of a memristive device. Under hard switching conditions, the loop area assumes the maximum value, decreasing for both directions.

For lower frequencies under $f = 50Hz$, in the soft switching behavior zone, the area decreases sharply until the loop collapses. For moderate to high frequency regime, plotting y against x reveals the characteristic hysteresis loop

For increasing values of the applied frequency, specially after $f = 120Hz$, the loop changes from sharp to smooth behaviors. The sharp behavior in a memcapacitor should occur with its physical limits approaching the boundaries.

Decreasing further the frequency of the driving signal will lead to the partial collapse of the hysteretic behavior. For these cases, switching occurs only once, leaving the device in its on state. For higher frequencies, the loop displays a smooth behavior as a result from soft switching conditions. Increasing further the frequency leads to the total collapse of the hysteretic behavior, by the appearance of a straight line in the hysteresis loop.

These behavioral changes can be captures from the plots of the loop area versus frequency.

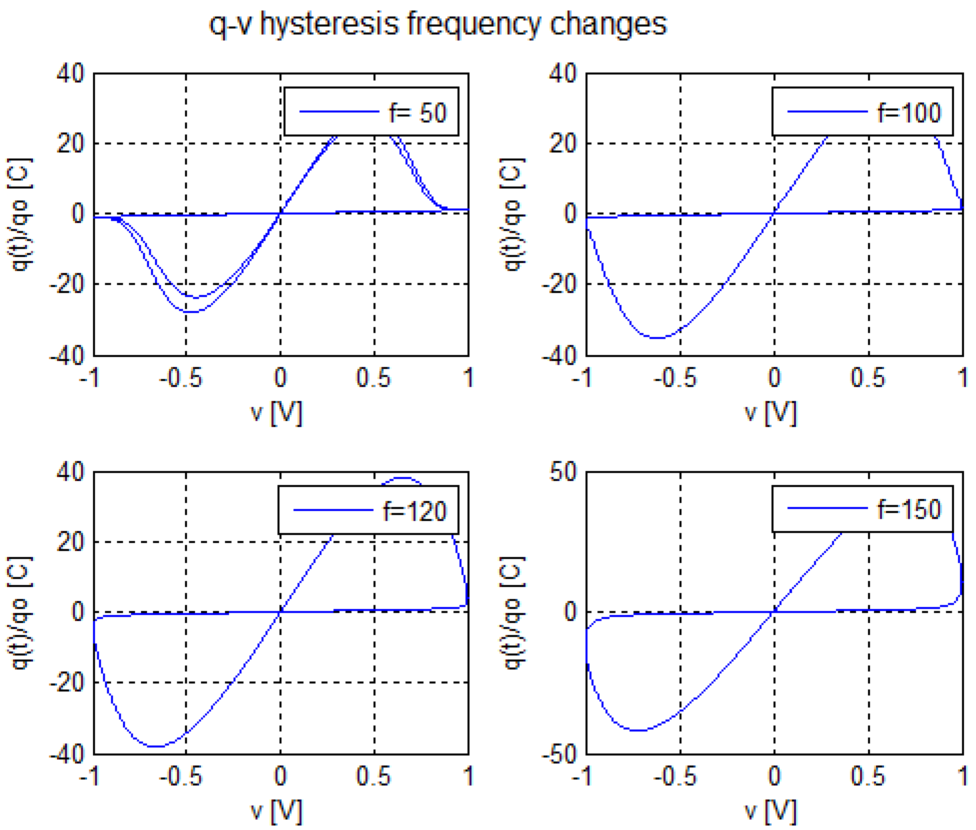


Figure 107 Hysteresis Plots for frequency changes in the First Model

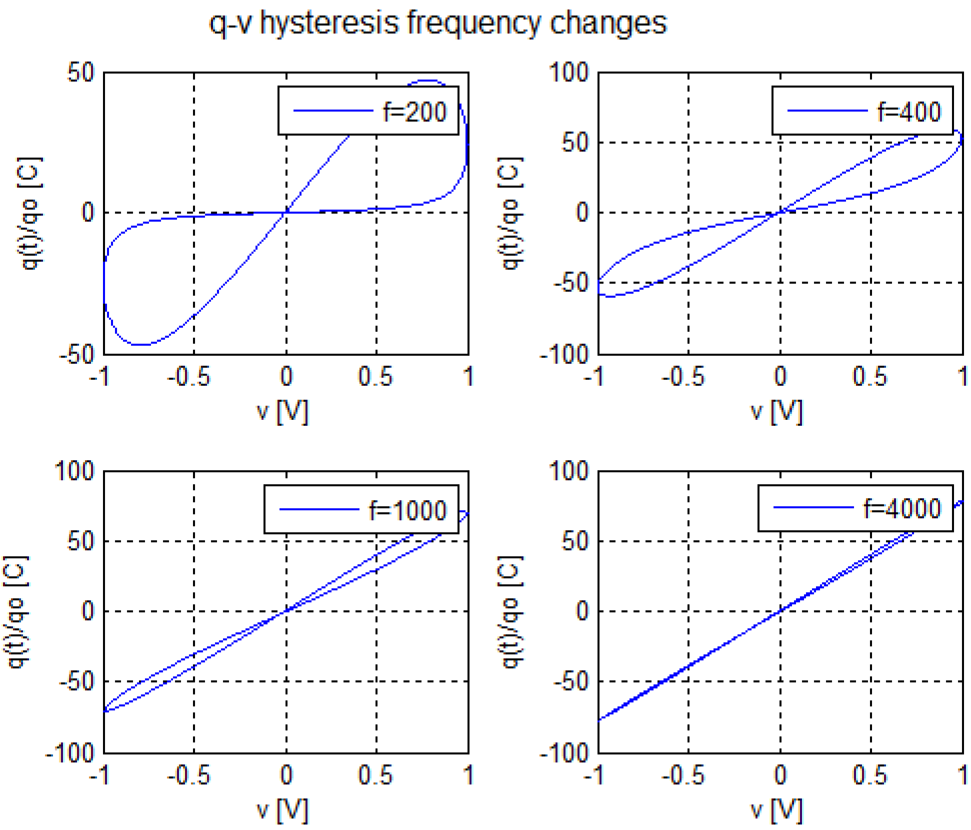


Figure 28 Further frequency changes for the First Model

Figures (29) and (30) show the variation of the normalized charge in function of time for the frequency sweep performed in this section. It is clearly seen the changes in the charge behavior near the frequencies of interest.

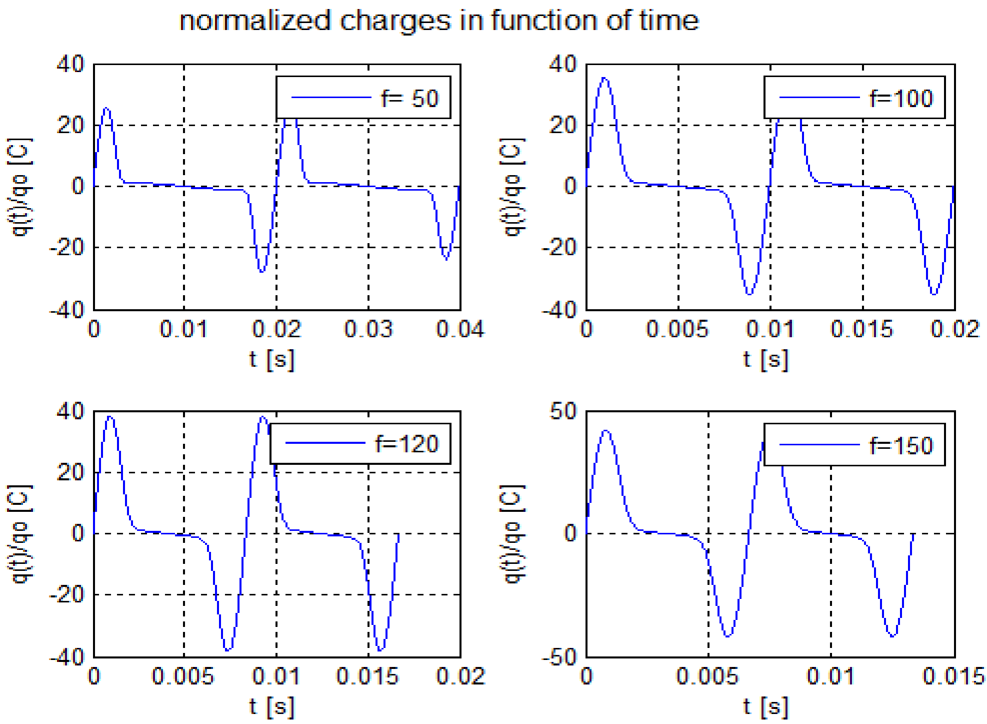


Figure 11 Normalized charge for frequency changes in the First Model

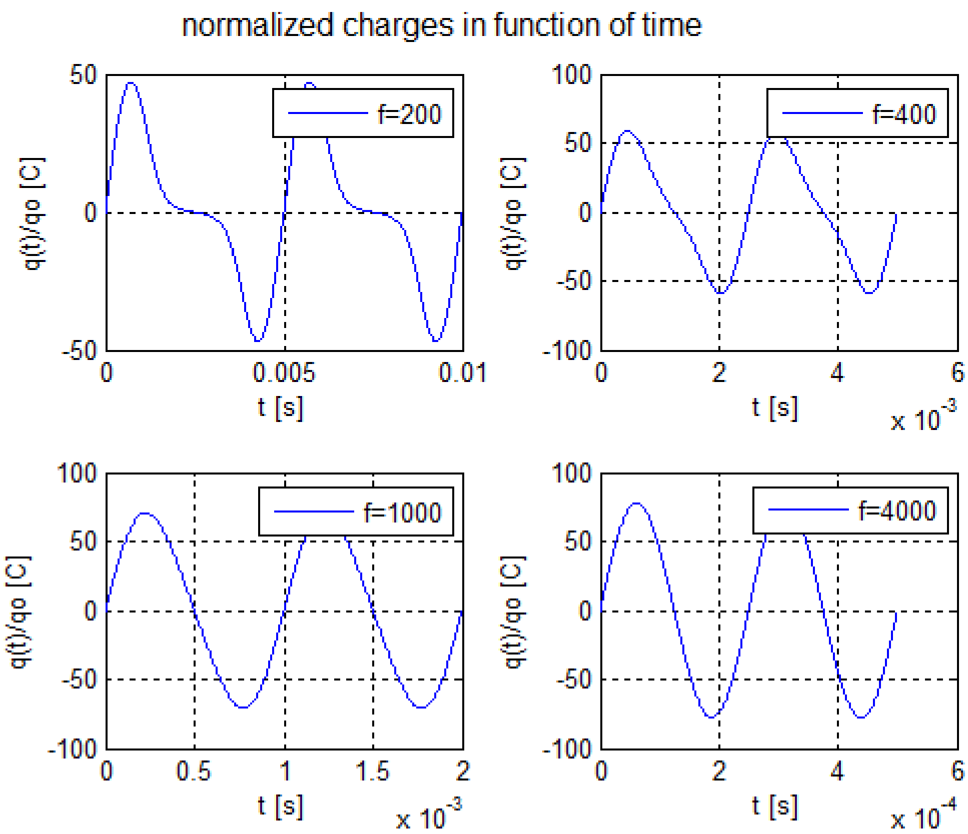


Figure 120 Normalized charge for further simulations for frequency changes in the First Model

Figures (31) and (32) show the normalized memcapacitances against voltage in a hysteretic loop. Again, the graphs are consistent with the values from which a *q-v* hysteresis plot are stable.

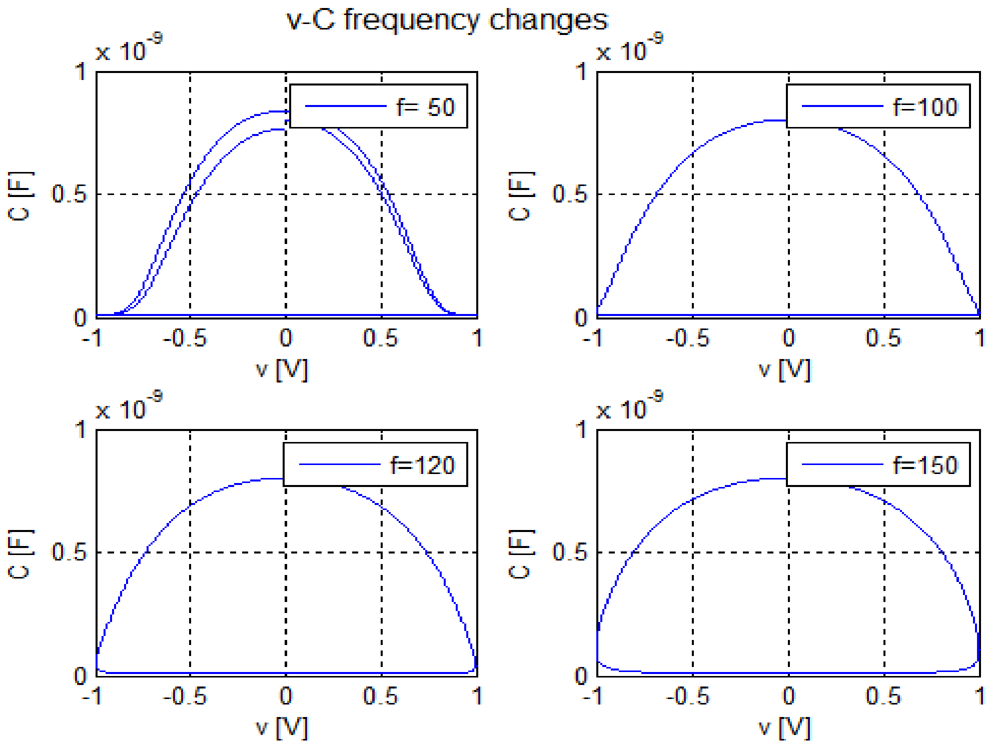


Figure 31 C-v Hysteresis plots for frequency variations of the First Model

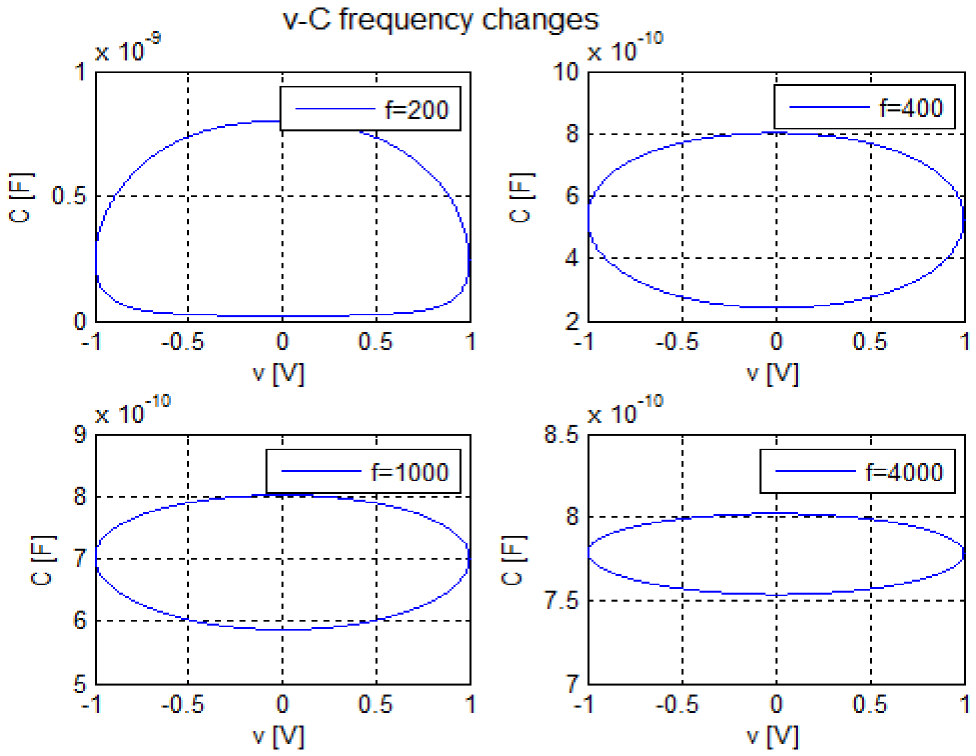


Figure 13 Frequency changes for C-v Hysteresis Loops

b) For the second model

As it can be seen in figure (33), the area plots degenerate into a straight line as frequency rises, which is consistent with the third fingerprint of a memristive device. Under hard switching conditions, the loop area assumes the maximum value, decreasing for both directions.

For lower frequencies under $f = 0.3Hz$, in the soft switching behavior zone, the area decreases sharply until the loop collapses. For moderate to high frequency regime, plotting *q* against *v* reveals the characteristic hysteresis loop.

For increasing values of the applied frequency, specially after $f = 0.9Hz$, the loop begins to degenerate into a straight line, according to the third fingerprint of a memcapacitor.

An interesting feature to be noticed is that the frequency ranges of which the memcapacitor model operate is far smaller than the first model. This happens because this model operates in a very fast switching mode, and it can be useful in applications where the frequency operation range and values are very low.

Figure (34) also shows the normalized charge in function of time, denoting this parameter is in accordance to the values of frequency from which a *q-v* hysteresis plot is found.

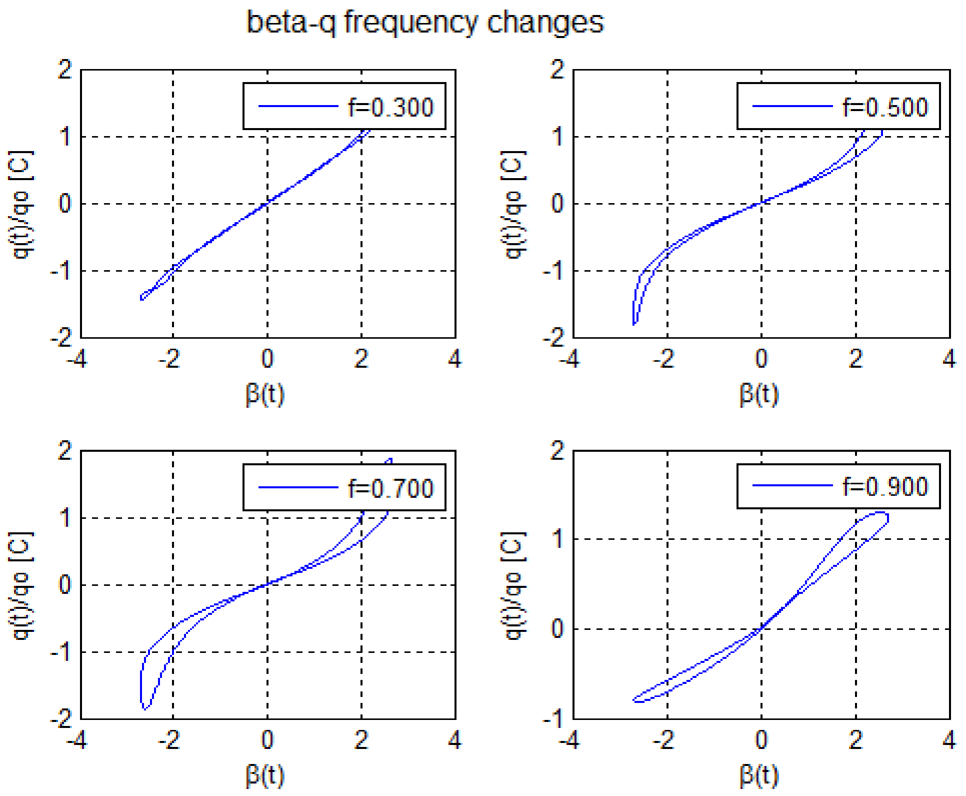


Figure 14 Hysteresis plots for frequency changes in the Second Model

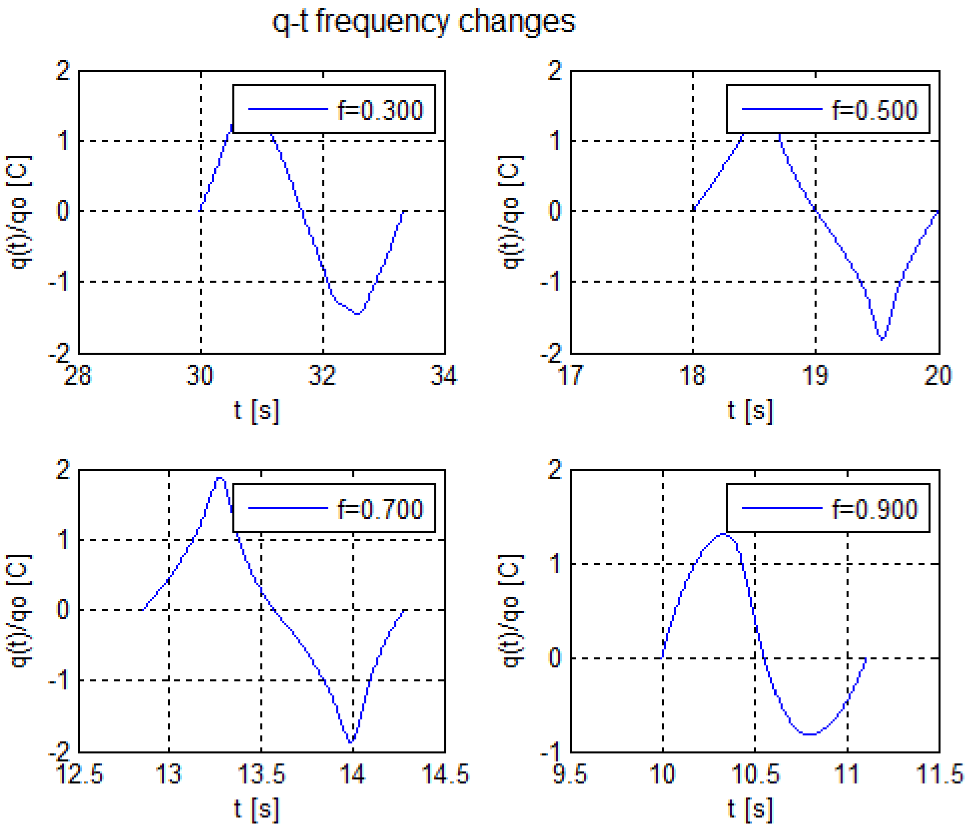


Figure 15 Normalized charge as a function of time for different frequencies for the Second Model

Figure (35) shows the *C-v* hysteresis plots for the range of frequencies used, once again consistent with the hysteresis found in the q-v plane.

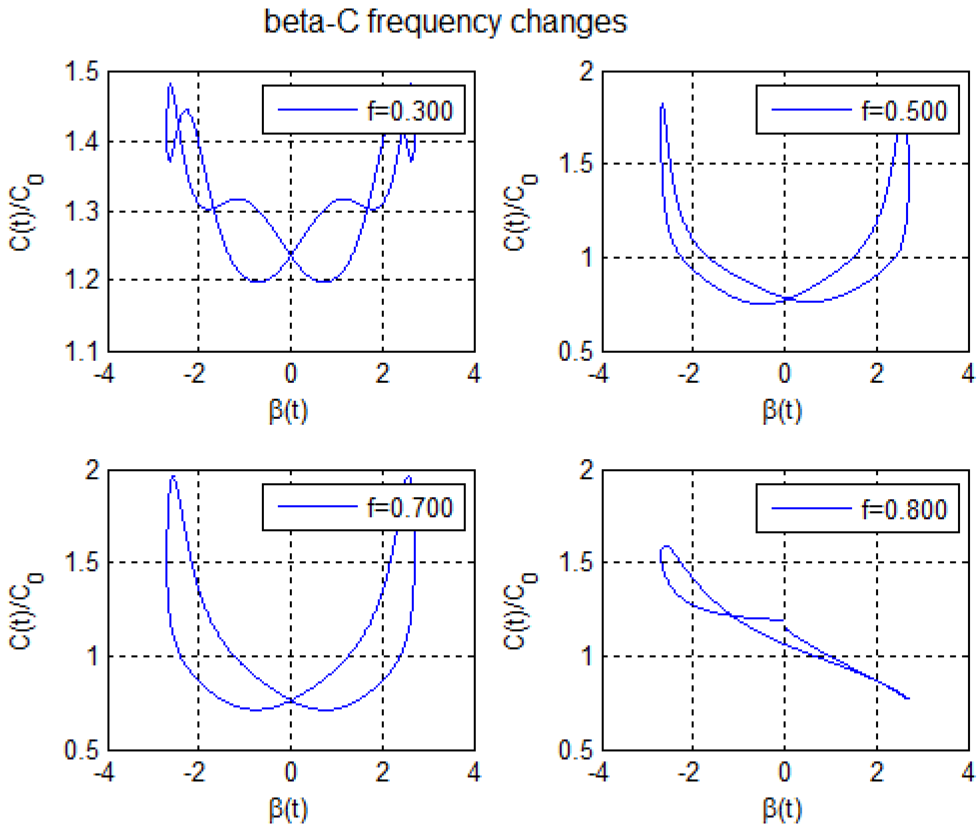


Figure 35 C-v hysteresis plots for frequency ranges of the Second Model

c) For the third model

As it can be seen in figure (36), the area plots degenerate into a straight line as frequency rises, which is consistent with the third fingerprint of a memristive device. Under hard switching conditions, the loop area assumes the maximum value, decreasing for both directions.

For lower frequencies under $f = 1Hz$, in the soft switching behavior zone, the area decreases sharply until the loop collapses. For moderate to high frequency regime, plotting *q* against *v* reveals the characteristic hysteresis loop.

For increasing values of the applied frequency, specially after $f = 1000Hz$, the loop begins to degenerate into a straight line, according to the third fingerprint of a memcapacitor.

Again, the graphs below show the symmetric nature of the charges Q_1 and Q_2.

For very high frequencies, as well as for very low ones, the MATLAB code enters in an infinite run time and does not converge into a solution.

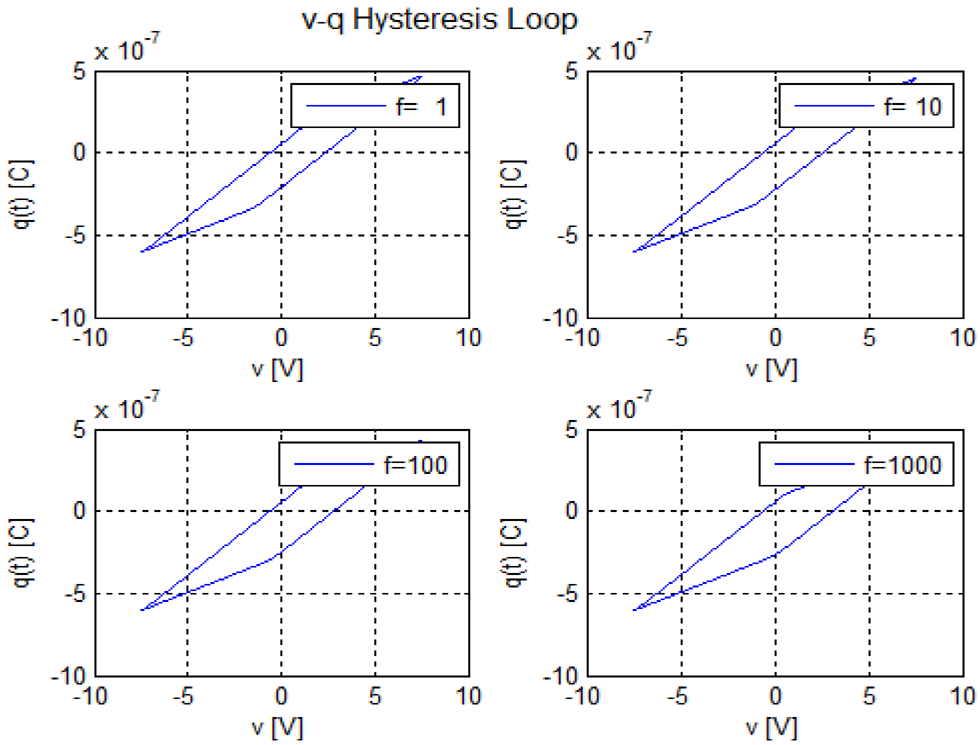


Figure 36 q-v Hysteresis Loop as frequency changes for the Third Model

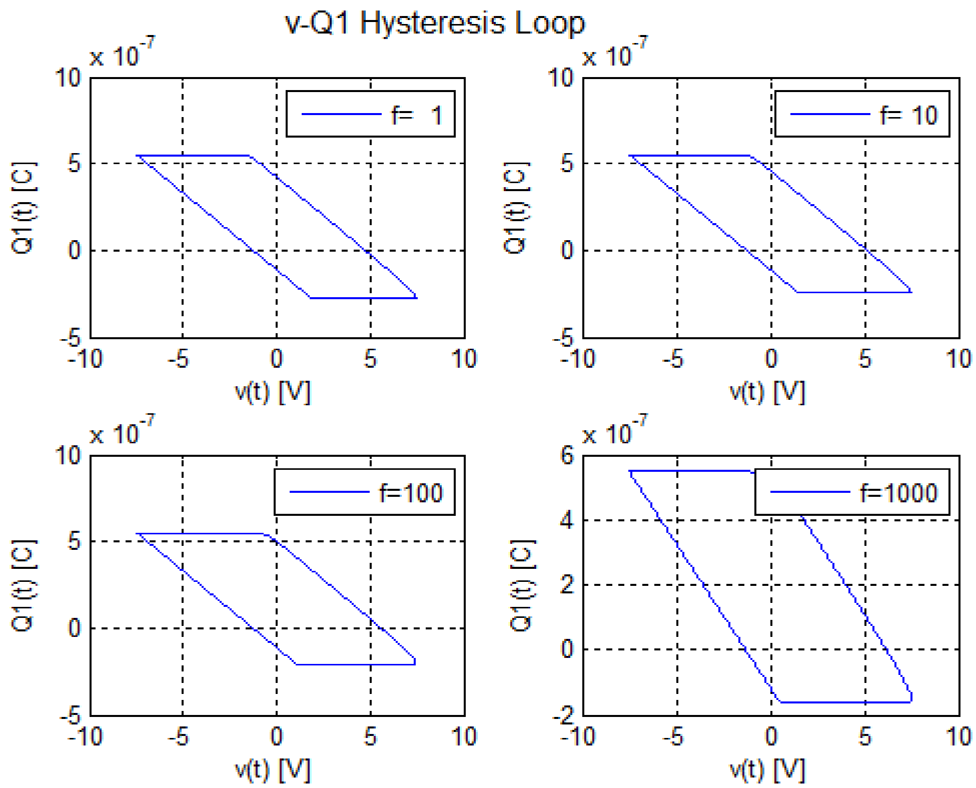


Figure 16 Q1-v Hysteresis loop as frequency changes for the Third Model

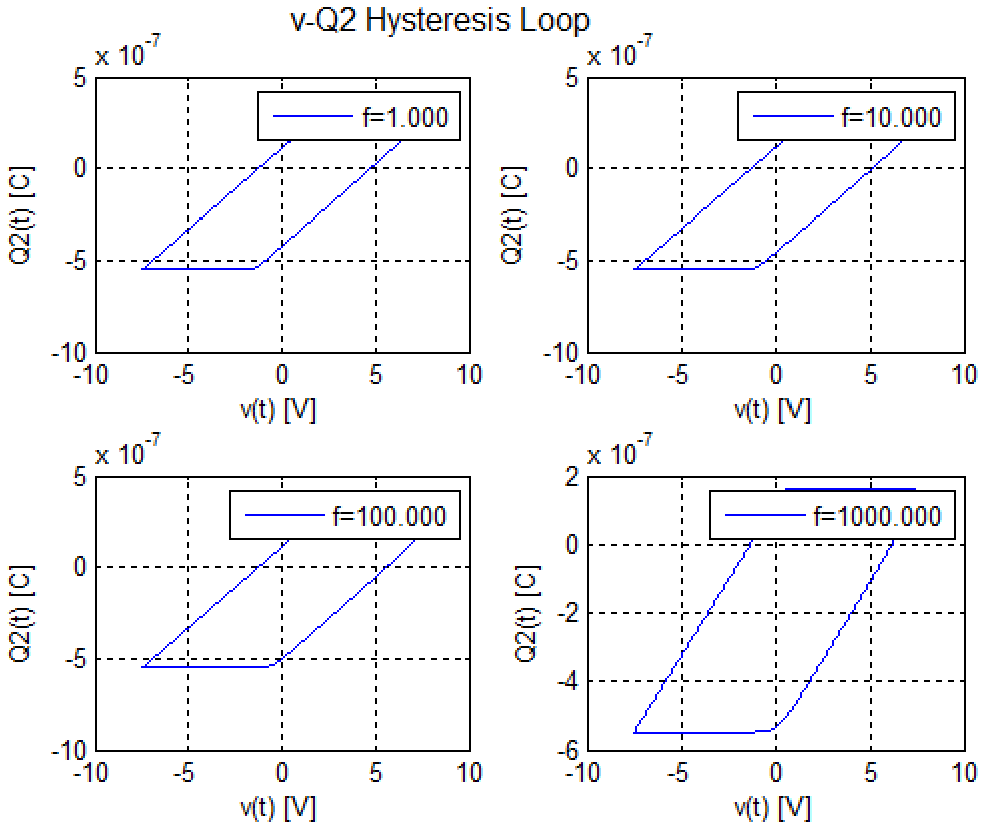


Figure 38 Q2-v Hysteresis Loop as frequency changes for the Third Model

Chapter Six: Conclusions

This work presented theories about the new memory capacitive device, the memcapacitor, its mathematical models and uses in the future of the nanotechnology and microelectronics. Here, three models of memcapacitive systems were presented, and a methodology of simulation in MATLAB by varying the frequency of the input voltage was conducted. With this information, it was possible to drawn the hysteresis plots for charge-voltage and capacitance-voltage for the models presented. Area of the plots were also taken from the data available, in order to drawn a full characterization of the mathematical models manipulated during the work.

From the data collected, it was possible to drawn the following conclusions:

First of all, it is expected to find the main hysteresis plot in the q-v plane, in accordance to the capacitive law q=Cv, once in opposition to the memristor, where the hysteresis plane is found in the v-I plane, which according to the Ohm's law;

Once the first theoretical model is the most predictable of all the ones studied, and showed to be well behaved for a certain range of values, it can serve as a table of comparison to the other two models studied here. All chaotic and irregular behavior the superlattice memcapacitive model and the elastic memcapacitive model showed was a deviation of the "smooth" theoretical model presented here.

This way, although assembled in the same theory (two conduction equations, one of them a state equation governed by a differential equation) and ruled by the same physical laws of electromagnetism, all the models studied presented different types of hysteresis plots: for the first model, a pinched type I hysteresis loop was found; For the third model an elliptical type II hysteresis loop was found because there must be a residual voltage drop in the device, and for other kinds of mathematical models of memcapacitor this is the pattern to be looked for.

In fact, the very presence of different forms of hysteresis loop just confirms the theory about memcapacitors and its variations in the *q-v* plane.

Talking about theory, once the three fingerprints of a memristive device was found in all three models studied, it is suffice to say that a memcapacitor and the models available in the literature nowadays are memristive systems.

The systems deviate considerably from the ideal model, represented by the first model studied. Hence it is suffice to conclude that different mathematical models are suitable for different applications once the frequency operation range differs from one another. While the first and third models operate at high frequencies, the second model operates at low frequencies. It is up to the circuit designer to match the model and the consequent frequency range to the desired use he/she needs;

Each model has its critical frequency, where the non-linear model degenerates into a linear hysteresis loop according to the fingerprints of a memory device. It is also a good specification the circuit designer must take into account in order to use the semiconductor device when it becomes available in Integrated Circuit, fact that the author believes to happen in a near future;

The state-of-the art presented in the literature predicts that the development of memory devices, especially in the particular case of the memcapacitors, will revolutionize the world of the electronics, first by breaking the cycle of the Moore's Law; then, by replacing the old methods to think and design memories in portable devices, making thus appear smaller, faster, and more efficient electronics devices in the market, with the philosophy of environment preservation by replacing the power sources in the electronics devices for a semiconductor new device with no power source. This concepts will give electronics a few more decades of economic domination over other technologies inside the field of electronics engineering, such as optoelectronics. There is no limits electronics can do and reach in the history of mankind.

5.2. Future Work

As a future work to be done in this subject, the author suggest more amplitude and frequency sweeps to be done, but this time, by varying physical features of a system, as well as by using more window functions, future researchers can extract figures of merit, such as rate of decay of the loops, operational bandwidth, among others.

the author also suggest an equivalent memcapcitor circuit to be constructed, by using the traditional lumped circuit elements, such as resistors and capacitors, maybe controlled by an Arduino or PIC microprocessor, in order to generate the hysteresis plots and compare them to the theoretical results achieved by this work, validating thus the theory. Circuit models drawn in CADs like *Pspice*, *Orcad* and *Labview* would be an interesting contribute to the theory and further implementation of an emulator circuit.

Surely, with advanced research and with an advanced materials laboratory available, a solid-state sample of memcapacitor should appear in upcoming years or decades. So an attempt to bring a two-terminal solid-state device as already made by the memristors is an exciting field of research for those who hold interest in the subject.

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Annexes

A.1. Matlab Code for the First Model

a) Fmemstate.m

```
function dx=Fmemstate(t,x)
global A p Con Coff k vo w
dx(1)=1;
xaux=x(2);
if xaux>1
   xaux=1;
end
if xaux<0
   xaux=0;
end
Fx=A*(1-((xaux-1/2)^2+3/4)^p);
v=vo*sin(w*x(1));
% C=Coff-(Coff-Con)*x(2);
dx(2)=k*Fx*v;
if (dx(2) < 0 && x(2) < 0)
   dx(2) = 0 ;
end
if (dx(2) > 0 && x(2) > 1)
   dx(2) = 0 ;
end
dx=dx';
```

b) AmplitudeChanges .m

```
%% description of the code
% amplitude changes in the memcapacitor
% third type I model
%%
clear all
close all
clc
%% data
voArray = [1,10,100,1000];
f=1000;
w = 2*pi*f;
%% plots
for counter1 = 1:length(voArray)
   vo = voArray(counter1);
   input = [f,vo];
   [output] = ODEsolution(input);
   sz = length(output(1,:));
   t(counter1,1:sz) = (output(1,:));
   x(counter1,1:sz) = (output(2,:));
   C(counter1,1:sz) =(output(3,:));
   v(counter1,1:sz) =(output(4,:));
```

```
    q(counter1,1:sz) =(output(5,:));
    qo(1)= (output(6,1));
    sprintf('passou %d vezes', counter1)
end

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(t(counter2,:),v(counter2,:));
    grid on;
    xlabel('t [s]');
    ylabel('v(t) [V]');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(t(counter2,:),q(counter2,:)/qo);
    grid on;
    xlabel('t [s]');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(v(counter2,:),q(counter2,:)/qo);
    grid on;
    xlabel('v [V]');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%3d','f=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
%set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(v(counter2,:),C(counter2,:));
    grid on;
    xlabel('v [V]');
```

```
    ylabel('C [F]');
    leg=sprintf('%s%3d','f=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',10)
```

c) FrequencyChanges.m

```
%% description of the code
% frequency changes in the memcapacitor
% third type I model
%%
clear all
close all
clc
%% data
fArray = [1,10,100,500];
vo=1;
w = 2*pi*fArray;
%% plots
for counter1 = 1:length(fArray)
    f = fArray(counter1);
    input = [f,vo];
    [output] = ODEsolution(input);
    sz = length(output(1,:));
    t(counter1,1:sz) = (output(1,:));
    x(counter1,1:sz) = (output(2,:));
    C(counter1,1:sz) =(output(3,:));
    v(counter1,1:sz) =(output(4,:));
    q(counter1,1:sz) =(output(5,:));
    qo(1)= (output(6,1));
    sprintf('passou %d vezes', counter1)
end

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
    plot(t(counter2,:),v(counter2,:));
    grid on;
    xlabel('t [s]');
    ylabel('v(t) [V]');
    leg=sprintf('%s%3d','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
```

```
    plot(t(counter2,:),q(counter2,:)/qo);
    grid on;
    xlabel('t [s]');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%3d','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
    plot(v(counter2,:),q(counter2,:)/qo);
    grid on;
    xlabel('v [V]');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%3d','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
%set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
    plot(v(counter2,:),C(counter2,:));
    grid on;
    xlabel('v [V]');
    ylabel('C [F]');
    leg=sprintf('%s%3d','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',10)
```

d) Area in dB

```
% Mem Device area study script
%
%
% Dynamics
% q=C(x)v
% dx/dt=kFx(x)v
%
% C(x) state-dependent capacitance mapping
% C(x)=Coff-(Coff-Con)x
%
% F(x) window function, to prevent x from becoming less than 0 or larger
% than 1, using Prodromakis window
% Fx(x)=A(1-((x-1/2)^2+3/4)^p)
```

```
%
% Area is computed using the v/i loop and Green Theorem.
% Memdevices modelled with Prodromakis window and HP dynamics
are symmetric
% then, the area of the loop is simply
%
% Area=2*integral(0,T/2,i*dv/dt)
%
% which must consider stationary device regime, excluding the initial
% period(s)
%
%%
clc
clear all
close all
% Model parameters
global A p Con Coff k vo f dt Tfinal w
% Window parameters
A=1;
p=5;
% Device parameters
Con=10e-12;                % Con capacitance
Coff=1e-9;                 % Coff capacitance
k=1000;          % process parameter
xo=0.2;                    % initial state
% stimulus parameters
vo=1;
f=1000;                           % stimulus frequency in Hz
% Note: the critical frequenct«y is around 50Hz for k=1000
w=2*pi*f;                         % angular frequency
Ns=100001;                 % time samples
N=100;                     % frequency samples
qo=Con*vo;
xo=0.5;
%%
% Incialization
Area=zeros(1,N);
wspace=logspace(1,5,N);
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
for n=1:N
   w=wspace(n);
   Tfinal=4*pi/w;
   dt=Tfinal/(Ns-1);
   t=0:dt:Tfinal;
   % Integration
   [tout, x]=ode15s(@Fmemstate,t,[0 xo],options);
   C=Coff-(Coff-Con)*x(:,2)';
   v=vo*sin(w*tout');
   q=C.*v;
   % second period
```

```
    q=q((Ns+1)/2:end);
    v=v((Ns+1)/2:end);
    % time derivatives of v(t)
    dv=zeros(1,(Ns+1)/2);
    dv(1)=v(1)-v(end);
    dv(2:end)=v(2:end)-v(1:end-1);
    % area integration - Green theorem: absolute value of the areas of the
    % two lobes. Note: Biolek and Corinto window functions may exhibit
    % different hard switching dynamics, which may constrain the ideal
    % periodic behaviour of M(q). For these cases integration must be
    % performed over the entire period of v(t), as shown below.

Area(n)=abs(q(:,1:(Ns+3)/4)*dv(:,1:(Ns+3)/4)')+abs(q(:,(Ns+3)/4:end)*dv(:
,(Ns+3)/4:end)');
end
semilogx(wspace,20*log10(Area/qo))
grid on
xlabel('\omega (rad/s)')
ylabel('Area')
title('Area in dB of Type I Theoric Model')
```

e) Memdevice_view.m

```
% Mem Device study script
%
% Dynamics
% q=C(x)v
% dx/dt=kFx(x)v
%
% C(x) state-dependent capacitance mapping
% C(x)=Coff-(Coff-Con)x
%
% F(x) window function, to prevent x from becoming less than 0 or larger
% than 1, using Prodromakis window
% Fx(x)=A(1-((x-1/2)^2+3/4)^p)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
clc
clear all
close all
% Model parameters
global A p Con Coff k vo f dt Tfinal w
% Window parameters
A=1;
p=5;
% Device parameters
Con=10e-12;                    % Con capacitance
Coff=1e-9;                     % Coff capacitance
k=1000;           % process parameter
xo=0.2;                   % initial state
```

```
% stimulus parameters
vo=1;
f=1000;                          % stimulus frequency in Hz
% Note: the critical frequency is around 50Hz for k=1000
w=2*pi*f;                        % angular frequency
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%
% Incialization
N=100001;
Tfinal=2/f;
dt=Tfinal/(N-1);
t=0:dt:Tfinal;
% Integration
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
[tout, x]=ode15s(@Fmemstate,t,[0 xo],options);
C=Coff-(Coff-Con)*x(:,2);
v=vo*sin(w*tout);
q=C.*v;
qo=Con*vo;
figure(1)
subplot(1,2,1)
plot(tout,v,tout,q/qo)
grid on
legend('v(t)','q(t)')
xlabel('t')
subplot(1,2,2)
plot(v,q/qo)
grid on
xlabel('v')
ylabel('q')
figure(2)
plot(v,C)
grid on
xlabel('v(t)')
ylabel('C(t)')
```

f) vsweep.m

```
% Mem Device area study script
% Dynamics
% q=C(x)v
% dx/dt=kFx(x)v
%
% C(x) state-dependent capacitance mapping
% C(x)=Coff-(Coff-Con)x
%
% F(x) window function, to prevent x from becoming less than 0 or larger
% than 1, using Prodromakis window
% Fx(x)=A(1-((x-1/2)^2+3/4)^p)
%
```

```
% Area is computed using the v/i loop and Green Theorem.
% Memdevices modelled with Prodromakis window and HP dynamics
are symmetric
% then, the area of the loop is simply
%
% Area=2*integral(0,T/2,i*dv/dt)
%
% which must consider stationary device regime, excluding the initial
% period(s)
%
%%
clc
clear all
close all
% Model parameters
global A p Con Coff k vo f dt Tfinal w
% Window parameters
A=1;
p=5;
% Device parameters
Con=10e-12;                % Con capacitance
Coff=1e-9;                 % Coff capacitance
k=1000;          % process parameter
xo=0.2;                  % initial state
% stimulus parameters
vo=1;
f=1000;                        % stimulus frequency in Hz
% Note: the critical frequenct«y is around 50Hz for k=1000
w=2*pi*f;                      % angular frequency
Ns=100001;                 % time samples
N=100;                 % frequency samples
qo=Con*vo;
xo=0.5;
%%
% Incialization
Area=zeros(1,N);
vspace=logspace(0,1,N);
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
for n=1:N
   vo=vspace(n);
   Tfinal=4*pi/w;
   dt=Tfinal/(Ns-1);
   t=0:dt:Tfinal;
   % Integration
   [tout, x]=ode15s(@Fmemstate,t,[0 xo],options);
   C=Coff-(Coff-Con)*x(:,2)';
   v=vo*sin(w*tout');
   q=C.*v;
   % second period
   q=q((Ns+1)/2:end);
```

```
    v=v((Ns+1)/2:end);
    % time derivatives of v(t)
    dv=zeros(1,(Ns+1)/2);
    dv(1)=v(1)-v(end);
    dv(2:end)=v(2:end)-v(1:end-1);
    % area integration - Green theorem: absolute value of the areas of the
    % two lobes. Note: Biolek and Corinto window functions may exhibit
    % different hard switching dynamics, which may constrain the ideal
    % periodic behaviour of M(q). For these cases integration must be
    % performed over the entire period of v(t), as shown below.

  Area(n)=abs(q(:,1:(Ns+3)/4)*dv(:,1:(Ns+3)/4)')+abs(q(:,(Ns+3)/4:end)*dv(:
  ,(Ns+3)/4:end)');
    fprintf('passou %d vezes\n',n);
  end
  semilogx(vspace,20*log10(Area/qo))
  grid on
  xlabel('vo (V)')
  ylabel('Area')
  title('Area in dB of Type I Theoric Model')
```

A.2. Matlab Code for the Second Model

a) Memdevice_view.m

```
% Mem Device study script
%
% Dynamics
% q(t)/qo=v(t)/(1+y)
% d2y/dt2+Gamma*dy/dt+4*pi*pi*y((y/y0)^2-1)+(beta(t)/(1+y))^2=0
%
% State variables
% x1=y
% x2=dy/dt
% State equations
% dx1/dt=x2
% dx2/dt=-(Gamma*dy/dt+4*pi*pi*y((y/y0)^2-1)+(beta(t)/(1+y))^2)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
clc
clear all
close all
% Model parameters
global beta0 Gamma y0 v0 k
% Device parameters
y0=0.2;     % No change
Gamma=0.7;  % No change
beta0=2.7;  % Can change slightly, chaotic for ]2.25, 2.58[
% initial state
xo=[0 0 0];
% stimulus parameters
```

```
vo=1;
k=0.5;                    % w/w0
f=k;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Incialization
N=1000000;
Tfinal=10/f;
dt=Tfinal/(N-1);
t=0:dt:Tfinal;
% Integration
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
[tout, x]=ode15s(@Fmemstate,t,xo,options);
v=vo*sin(2*pi*k*tout);
beta=beta0*sin(2*pi*k*tout);
q=v./(1+x(:,2));
tout=tout(9*N/10:end);
v=v(9*N/10:end);
beta=beta(9*N/10:end);
q=q(9*N/10:end);
figure(1)
subplot(1,2,1)
plot(tout,beta,tout,q)
grid on
legend('\beta(t)','q(t)/q_0')
xlabel('t')
subplot(1,2,2)
plot(beta,q)
grid on
xlabel('\beta')
ylabel('q/q_0')
figure(2)
plot(beta,q./v)
grid on
xlabel('\beta(t)')
ylabel('C(t)/C_0')
```

b) Fmemstate.m

```
function dx=Fmemstate(t,x)
global beta0 Gamma y0 v0 k
dx(1)=1;
dx(2)=x(3);
beta=beta0*sin(2*pi*k*x(1));
dx(3)=-(Gamma*x(3)+4*pi*pi*x(2).*((x(2)/y0).^2-1)+(beta./(1+x(2))).^2);
dx=dx';
```

c) MultipleFmemstate.m

```
function dx=MultipleFmemstate(t,x,inputs)
global beta0 Gamma y0 v0 k
```

```
fo=inputs(1);
%vo=inputs(2);
%%
dx(1)=1;
dx(2)=x(3);
beta=beta0*sin(2*pi*fo*x(1));
dx(3)=-(Gamma*x(3)+4*pi*pi*x(2).*((x(2)/y0).^2-1)+(beta./(1+x(2))).^2);
dx=dx';
end
```

d) FrequencyChanges.m

```
clear all
close all
clc
%% data
fArray = [1,1.2,1.5,2];
vo=1;
w = 2*pi*fArray;
%% plots
for counter1 = 1:length(fArray)
   f = fArray(counter1);
   input = [f];
   [output] = ODEsolution(input);
   sz = length(output(1,:));
   t(counter1,1:sz) = (output(1,:));
   beta(counter1,1:sz) = (output(2,:));
   C(counter1,1:sz) =(output(3,:));
   v(counter1,1:sz) =(output(4,:));
   q(counter1,1:sz) =(output(5,:));
   sprintf('passou %d vezes', counter1)
end

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(t(counter2,:),beta(counter2,:));
   grid on;
   xlabel('t [s]');
   ylabel('beta(t)');
   leg=sprintf('%s%.2f','f=',fArray(counter2));
   legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(t(counter2,:),q(counter2,:));
   grid on;
```

```
    xlabel('t [s]');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%.2f','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
    plot(beta(counter2,:),q(counter2,:));
    grid on;
    xlabel('\beta(t)');
    ylabel('q(t)/qo [C]');
    leg=sprintf('%s%.2f','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
%set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
    subplot(2,length(fArray)/2,counter2);
    plot(beta(counter2,:),C(counter2,:));
    grid on;
    xlabel('\beta(t)');
    ylabel('C(t)/C_0');
    leg=sprintf('%s%.3f','f=',fArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',10)
```

e) ODEsolution.m

```
% Mem Device study script
%
% Dynamics
% q(t)/qo=v(t)/(1+y)
% d2y/dt2+Gamma*dy/dt+4*pi*pi*y((y/y0)^2-1)+(beta(t)/(1+y))^2=0
%
% State variables
% x1=y
% x2=dy/dt
% State equations
% dx1/dt=x2
% dx2/dt=-(Gamma*dy/dt+4*pi*pi*y((y/y0)^2-1)+(beta(t)/(1+y))^2)
%
function [output]= ODEsolution(input)
fo=input(1);
```

```
%vo=input(2);
%% data
% Model parameters
global beta0 Gamma y0 v0
% Device parameters
y0=0.2;     % No change
Gamma=0.7;  % No change
beta0=2.7;  % Can change slightly, chaotic for ]2.25, 2.58[

%% initial state
xo=[0 0 0];
%% stimulus parameters
vo=1;
%k=0.5;                    % w/w0
%f=k;
%% Incialization
N=1000000;
Tfinal=10/fo;
dt=Tfinal/(N-1);
t=0:dt:Tfinal;
%% Integration
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
eqInput = [fo];

[tout, x]=ode15s(@MultipleFmemstate,t,xo,options,eqInput);

v=vo*sin(2*pi*fo*tout);
beta=beta0*sin(2*pi*fo*tout);
q=v./(1+x(:,2));
tout=tout(9*N/10:end);
v=v(9*N/10:end);
beta=beta(9*N/10:end);
q=q(9*N/10:end);
%% outputs
output(1,:) = tout;
output(2,:) = beta;
output(3,:) = q./v; %C=q/v
output(4,:) = v;
output(5,:) = q;
end
```
f)

A.3. Matlab Code for the third Model

a) Memdevice_view.m

```
% Mem Device study script
%
% Dynamics
% dq/dt=v/R-q/RC
% dQ1/dt=-I1_2(v1,U)
```

```
% dQ2/dt=I1_2(v1,U)
% v1=(2q+Q1-Q2)/(2e0erS)
%
% State variables
% x1=t
% x2=q
% x3=Q1
% x4=Q2
% State equations
% dx1=1;
% dx2=v/R-q/RC
% dx3=-I1_2(v1,U)
% dx4=I1_2(v1,U)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
clc
clear all
close all
% Model parameters
global e0 er S d d1 U R Co vo f
% Physical constants
% h=4.1356674335e-15;  % Planck constant (eVs)
% h=6.62606957e-37;    % Planck constant (m^2g/s)
% e=1.60217656535e-19; % electron charge (C)
% me=9.1093821545e-34; % electron mass (g)
e0=8.854187817e-12;  % vacuum permitivitty (F/m)
% Device parameters
er=5;              % relative permitivitty
S=1e-4;            % plate area (m^2)
d=100e-9;          % plate separation (m)
d1=50e-9;          % internal plate separation (m)
U=0.33;            % Potential barrier height (eV)
R=1;               % Series resistance
Co=e0*er*S/d;      % Device capacitance
% initial state
xo=[0 0 0 0];
% stimulus parameters
vo=7.5;            % stimulus amplitude
f=1000;            % stimulus frequency
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Incialization
N=1000000;
Tfinal=10/f;
dt=Tfinal/(N-1);
t=0:dt:Tfinal;
% Integration
options = odeset('RelTol',1e-12,'AbsTol',1e-15);
[tout, x]=ode15s(@Fmemstate,t,xo,options);
```

```
v=vo*sin(2*pi*f*tout);
C=Co./(1+d1*x(:,3)./(d*x(:,2)));
q=x(:,2);
Q1=x(:,3);
Q2=x(:,4);
figure(1)
plot(t,q,t,Q1,t,Q2)
grid on
xlabel('t (s)')
ylabel('(q, Q1, Q2)')
legend('q(t)','Q_1(t)','Q_2(t)')
v=v(9*N/10:end);
t=tout(9*N/10:end);
q=x(9*N/10:end,2);
Q1=x(9*N/10:end,3);
Q2=x(9*N/10:end,4);
C=C(9*N/10:end);
figure(2)
plot(v,C)
xlabel('v(t) (V)')
ylabel('C(t) (F)')
grid on
figure(3)

plot(v,q,'r',v,Q1,'b',v,Q2,'g')
grid on
xlabel('v(t) (V)')
ylabel('q, Q_1, Q_2 (C)')
legend('q(t)','Q_1(t)','Q_2(t)')
```

b) Fmemstate.m

```
function dx=Fmemstate(t,x)
global e0 er S d d1 U R Co vo f
dx(1)=1;
if x(2)==0
   x(2)=1e-60;
end
C=Co/(1+d1*x(3)/(d*x(2)));
v=vo*sin(2*pi*f*x(1));
dx(2)=v/R-x(2)/(R*C);
v1=d1*(x(2)+x(3))/(e0*er*S);
dx(3)=-S*Jk(U,v1,d1);
dx(4)=-dx(3);
dx=dx';
end
```

c) jk.m

```
function jk=Jk(U,v,d)
% function jk=Jk(U,v,d)
% See Simmons paper for the contants The relevant equations are for a
```

```
% rectangular tunnel barrier (equations 27, 30 and corresponding 46 and 47,
% respectively)
A=6.2E10;
B=1.025;
C=3.38E10;
D=0.689;
d=d/1E-10; % convert m to angstrom
if v<=U
   jk=(A/(d^2))*((U-v/2)*exp(-B*d*sqrt(U-v/2))-(U+v/2)*exp(-B*d*sqrt(U+v/2)));
else
   F=v/d;
   jk=(C*(F^2)/U)*(exp(-D*(U^1.5)/F)-(1+2*v/U)*exp((-
D*(U^1.5)/F)*sqrt(1+2*v/U)));
end
jk=jk/0.0001; %convert A/cm^2 to A/m^2
end
```

d)Test_Jk.m

```
clc
clear all
close all
% Model parameters
global h e me e0 er S d d1 U R Co vo f
% Physical constants
% h=4.1356674335e-15;  % Planck constant (eVs)
% h=6.62606957e-37;    % Planck constant (m^2g/s)
% e=1.60217656535e-19; % electron charge (C)
% me=9.1093821545e-34; % electron mass (g)
e0=8.854187817e-12;  % vacuum permitivitty (F/m)
% Device parameters
er=5;              % relative permitivitty
S=1e-4;              % plate area (m^2)
d=100e-9;              % plate separation (m)
d1=5e-9;           % internal plate separation (m)
U=0.5;              % Potential barrier height (eV)
R=1;               % Series resistance
Co=e0*er*S/d;        % Device capacitance
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
vk=linspace(0,1.5,1000);
jk=zeros(1,1000);
for n=1:1000
   jk(n)=Jk(U,vk(n),d1);
end
semilogy(vk,jk)
axis([0 1.5 1e-6 1e5])
xlabel('v_k (V)')
ylabel('j_k (A/m^2)')
grid on
```

e) FrequencyChanges.m

```
%% description of the code
% frequency changes in the memcapacitor
% third type I model
%%
clear all
close all
clc
%% data
fArray = [1e4,1e5,1e6,1e7];
vo=7.5;
w = 2*pi*fArray;
%% plots
for counter1 = 1:length(fArray)
   f = fArray(counter1);
   input = [f,vo];
   [output] = ODEsolution(input);
   sz = length(output(1,:));
   t(counter1,1:sz) = (output(1,:));
   Q1(counter1,1:sz) = (output(2,:));
   Q2(counter1,1:sz) =(output(3,:));
   q(counter1,1:sz) =(output(4,:));
   C(counter1,1:sz) =(output(5,:));
   v(counter1,1:sz) =(output(6,:));
   sprintf('passou %d vezes', counter1)
end

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(t(counter2,:),v(counter2,:));
   grid on;
   xlabel('t [s]');
   ylabel('v(t)');
   leg=sprintf('%s%3d','f=',fArray(counter2));
   legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(v(counter2,:),q(counter2,:));
   grid on;
   xlabel('v [V]');
   ylabel('q(t) [C]');
   leg=sprintf('%s%3d','f=',fArray(counter2));
   legend(leg);
end
```

```
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(v(counter2,:),Q1(counter2,:));
   grid on;
   xlabel('v(t) [V]');
   ylabel('Q1(t) [C]');
   leg=sprintf('%s%3d','f=',fArray(counter2));
   legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
%set(h3,'FontSize',15)

figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(v(counter2,:),Q2(counter2,:));
   grid on;
   xlabel('v(t) [V]');
   ylabel('Q2(t) [C]');
   leg=sprintf('%s%.3f','f=',fArray(counter2));
   legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',10)
figure();
for counter2 = 1:length(fArray)
   subplot(2,length(fArray)/2,counter2);
   plot(v(counter2,:),C(counter2,:));
   grid on;
   xlabel('v(t) [V]');
   ylabel('C(t)');
   leg=sprintf('%s%3d','f=',fArray(counter2));
   legend(leg);
end
```

f) AmplitudeChanges.m

```
% description of the code
% amplitude changes in the memcapacitor
% third type I model
%%
clear all
close all
clc
%% data
voArray = [1,10,100,500];
f=1;
```

```
w = 2*pi*f;
%% plots
for counter1 = 1:length(voArray)
    vo = voArray(counter1);
    input = [f,vo];
    [output] = ODEsolution(input);
    sz = length(output(1,:));
    t(counter1,1:sz) = (output(1,:));
    Q1(counter1,1:sz) = (output(2,:));
    Q2(counter1,1:sz) =(output(3,:));
    q(counter1,1:sz) =(output(4,:));
    C(counter1,1:sz) =(output(5,:));
    v(counter1,1:sz) =(output(6,:));
    sprintf('passou %d vezes', counter1)
end

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(t(counter2,:),v(counter2,:));
    grid on;
    xlabel('t [s]');
    ylabel('v(t)');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
   plot(v(counter2,:),q(counter2,:));
    grid on;
    xlabel('v [V]');
    ylabel('q(t) [C]');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
   plot(v(counter2,:),Q1(counter2,:));
    grid on;
    xlabel('v(t) [V]');
    ylabel('Q1(t) [C]');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
```

```
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
%set(h3,'FontSize',15)

figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
 plot(v(counter2,:),Q2(counter2,:));
    grid on;
    xlabel('v(t) [V]');
    ylabel('Q2(t) [C]');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
% [ax4,h3]=suplabel('Frequency Changes for Type I Model' ,'t');
% set(h3,'FontSize',10)
figure();
for counter2 = 1:length(voArray)
    subplot(2,length(voArray)/2,counter2);
    plot(v(counter2,:),C(counter2,:));
    grid on;
    xlabel('v(t) [V]');
    ylabel('C(t)');
    leg=sprintf('%s%3d','vo=',voArray(counter2));
    legend(leg);
end
```